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Numerical Simulation of CO_2 Adsorption Behaviour of Polyaspartamide Adsorbent for Post-Combustion CO_2 Capture

Kelvin Odafe Yoro

(1230119)

A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Master of Science in Engineering.

Supervisor: Prof. Michael O. Daramola

Co-supervisor: Dr. Jean L. Mulopo

10 February, 2017.

Declaration

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

…….. …… day of……../…….

Signature of Candidate Day Month Year

Dedication

I dedicate this dissertation to God almighty, the giver and sustainer of life, who has been my help from ages past, my hope for years to come, my glory and the lifter of my head.

Abstract

Climate change due to the ever-increasing emission of anthropogenic greenhouse gases arising from the use of fossil fuels for power generation and most industrial processes is now a global challenge. It is therefore imperative to develop strategies or modern technologies that could mitigate the effect of global warming due to the emission of CO_2. Carbon capture and storage (CCS) is a viable option that could ensure the sustainable use of cheap fossil fuels for energy generation with less CO_2 emission. Amongst existing CCS technologies, absorption technology using monoethanolamine (MEA) is very mature and widely embraced globally. However, the absorption technology has a lot of challenges such as, low CO_2 loading, high energy requirement for solvent regeneration, corrosive nature etc. On this note, the adsorption technology using solid sorbents is being considered for CO_2 capture due to its competitive advantages such as flexibility, low energy requirement for sorbent regeneration, non-corrosive nature etc. On the other hand, adsorbents have a very vital role to play in adsorption technology and there is need to understand the behaviour of adsorbents for CO_2 capture under different operating conditions in order to adapt them for wider applications. On this note, the study contained in this dissertation investigated the adsorption behaviour of a novel polymer-based adsorbent (polyaspartamide) during post-combustion CO_2 capture using experimental study and mathematical modelling approach.

Polyaspartamide is an amine-rich polymer widely used in drug delivery. In addition, its rich amine content increases its affinity for CO_2. Its porosity, thermal stability and large surface area make it a promising material for CO_2 capture. In view of this, polyaspartamide was used as the adsorbent for post-combustion CO_2 capture in this study. This dissertation investigated the kinetic behaviour, the diffusion mechanism and rate limiting steps (mass transfer limitation) controlling the CO_2 adsorption behaviour of this adsorbent. Furthermore, effect of impurities such as moisture and other operating variables such as temperature, pressure, inlet gas flow rate etc. on the CO_2 adsorption behaviour of polyaspartamide was also investigated. Existing mathematical models were used to understand the kinetics and diffusion limitation of this adsorbent during CO_2 capture. Popularly used gas-solid adsorption models namely; Bohart-Adams and Thomas model were applied in describing the breakthrough curves in order to ascertain the equilibrium concentration and breakthrough time for CO_2 to be adsorbed onto

polyaspartamide. Lagergren's pseudo 1st and 2nd order models as well as the Avrami kinetic models were used to describe the kinetic behaviour of polyaspartamide during post-combustion CO_2 capture. Parameter estimations needed for the design and optimization of a CO_2 adsorption system using polyaspartamide were obtained and presented in this study. The Boyd's film diffusion model comprising of the interparticle and intra-particle diffusion models were used to investigate the effect of mass transfer limitations during the adsorption of CO_2 onto polyaspartamide.

Data obtained from continuous CO_2 adsorption experiments were used to validate the models in this study. The experiments were conducted using a laboratory-sized packed-bed adsorption column at isothermal conditions. The packed bed was attached to an ABB CO_2 analyser (model: ABB-AO2020) where concentrations of CO_2 at various operating conditions were obtained.

The results obtained in this study show that temperature, pressure and gas flow rate had an effect on the adsorption behaviour of polyaspartamide (PAA) during CO_2 capture. Polyaspartamide exhibited a CO_2 capture efficiency of 97.62 % at the lowest temperature of 303 K and pressure of 2 bar. The amount of CO_2 adsorbed on polyaspartamide increased as the operating pressure increased and a decrease in the adsorption temperature resulted in increased amount of CO_2 adsorbed by polyaspartamide. The amounts of CO_2 adsorbed on polyaspartamide were 5.9, 4.8 and 4.1 mol CO_2/kg adsorbent for adsorption temperatures of 303, 318 and 333 K, respectively.

The maximum amount of CO_2 adsorbed by polyaspartamide at different flow rates of 1.0, 1.5 and 2.5 ml/s of the feed gas were 7.84, 6.5 and 5.9 mmol CO_2/g of adsorbent. This shows that higher flow rates resulted in decreased amount of CO_2 adsorbed by polyaspartamide because of low residence time which eventually resulted in poor mass transfer between the adsorbent and adsorbate. Under dry conditions, the adsorption capacity of polyaspartamide was 365.4 mg CO_2/g adsorbent and 354.1 mgCO_2/g adsorbent under wet conditions. Therefore, the presence of moisture had a negligible effect on the adsorption behaviour of polyaspartamide. This is very common with most amine-rich polymer-based adsorbents. This could be attributed to the fact that CO_2 reacts with moisture to form carbonic acid, thereby enhancing the CO_2 adsorption capacity of the material.

In conclusion, this study confirmed that the adsorption of CO_2 onto polyaspartamide is favoured at low temperatures and high operating pressures. The adsorption of CO_2 onto polyaspartamide was governed by film diffusion according to the outcome of the Boyd's film diffusion model. It was also confirmed that intra-particle diffusion was the rate-limiting step controlling the adsorption of CO_2 onto polyaspartamide. According to the results from the kinetic study, it can be inferred that lower temperatures had an incremental effect on the kinetic behaviour of polyaspartamide, external mass transfer governed the CO_2 adsorption process and the adsorption of CO_2 onto polyaspartamide was confirmed to be a physicochemical process (both physisorption and chemisorption).

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Publications and Presentations

The following journal articles and conference papers were written from this present work.

Publications:

1. **Yoro, K.O**., Singo, M., Mulopo, J.L., Daramola, M.O., Modelling and Experimental Study of the CO_2 Adsorption Behaviour of Polyaspartamide as an Adsorbent during Post-Combustion CO_2 Capture, *Energy Procedia,* 2017, *XX: XX–XXX*. ***(Manuscript submitted).***

2. **Yoro, K.O**., Sekoai, P.T., The Potential of CO_2 Capture and Storage Technology in South Africa's Coal-Fired Thermal Power Plants, *Environments,* 2016, 3, 24.

3. Sekoai P.T., **Yoro, K.O**., Biofuel Development Initiatives in Sub-Saharan Africa: Opportunities and Challenges, *Climate*, 2016, 4(2), 33.

4. **Yoro, K.O**., Mulopo, J.L., Daramola, M.O., Investigating the Diffusion Mechanism and Rate-limiting Step during the Adsorption of CO_2 from a CO_2/N_2 mixture using a Novel Polyaspartamide Material as an Adsorbent. ***(Manuscript in preparation)***.

5. **Yoro, K.O**., Mulopo, J.L., Daramola, M.O., Effect of Moisture and Operating Variables on the CO_2 Adsorption Capacity of Polyaspartamide Adsorbent during Post-Combustion CO_2 Capture: A Modelling Approach. ***(Manuscript in preparation)***.

Conference presentations and proceedings:

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2. **Yoro, K.O.,** Mulopo, J.L., Daramola, M.O., Effect of Moisture and Other Operating Variables on the CO_2 Adsorption Capacity of Polyaspartamide (PAA) during Post-Combustion CO_2 Capture. – **Oral presentation,** *International Conference on Environment, Materials and Green Technology*, 24-25th November 2016 - VUT Southern Gauteng Science & Technology Park– Educity Campus, South Africa.

3. **Yoro, K.O.,** Singo, M., Mulopo, J.L., Daramola, M.O., Modelling and Experimental Study of the CO_2 Adsorption Behaviour of Polyaspartamide as an Adsorbent during Post-Combustion CO_2 Capture- **Poster presentation**, *International conference on greenhouse gas control technologies (GHGT-13),* 14th – 18th November 2016, SwissTech Convention Center - Lausanne, Switzerland.

4. **Yoro, K.O**., Daramola, M.O., Mulopo, J.L., Sustainable use of Coal for Energy Production in South Africa with less CO_2 Emission: CO_2 Capture and Storage a promising option- **Oral presentation**, *Renewable and sustainable Energy Postgraduate symposium,* 4th -6th September 2016., University of Fort Hare, Alice, Eastern Cape, South Africa.

5. **Yoro, K.O**., Singo, M., Daramola, M.O., Mulopo, J.L., Mathematical Modelling of Adsorption Behaviour of Sod-ZMOF/Chitosan Adsorbent during Post-Combustion CO_2 Capture, ISBN #: 1-890977-33-0 - **Oral Presentation**, *33rd International Pittsburgh Coal Conference,* 8th – 12th August 2016, Cape Town, South Africa.

6. **Yoro, K.O**., Daramola, M.O., Mulopo, J.L., Numerical simulation of the adsorption behaviour of polyaspartamide during post combustion CO_2 capture- **Oral presentation**, *6th National Students colloquium on Clean coal, Carbon, Energy and the environment,* 30th June 2015, University of the Witwatersrand Sports Administration Building, Sturrock Park, Braamfontein, Johannesburg, South Africa.

7. South African Centre for carbon capture & storage, SACCCS 4th CCS Conference 20th- 21st October 2015, Capital 20 West hotel, Sandton, Johannesburg, South Africa. (**Delegate**)

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Nomenclature

% E Percentage Error

C Final concentration of CO_2

CCS Carbon capture and storage

C_e Concentration of CO_2 at equilibrium

C_o Initial concentration of CO_2

EDA Ethylene Diamine

K_A Avrami constant (s^{-1})

K_f Pseudo 1st order constant (S^{-1})

K_s Pseudo 2nd order constant ($gmol^{-1}s^{-1}$)

N Number of experimental runs

nA Avrami exponent

PAA Polyaspartamide

qe Amount of CO_2 adsorbed at equilibrium ($mol\ g^{-1}$)

Q_{Exp} Amount of CO_2 adsorbed from experiment ($mol\ g^{-1}$)

Q_{mod} Amount of CO_2 adsorbed predicted by the model ($mol\ g^{-1}$)

q_t Amount of CO_2 adsorbed at a particular time ($mol\ g^{-1}$)

t Time (seconds)

VSA Vacuum swing adsorption

X- Mass of adsorbent

CHAPTER ONE

General Introduction

1.1 Motivation and Background

Environmental issues due to the tremendous consumption of fossil fuels are raising serious global concerns today; especially the emission of carbon dioxide which is a major anthropogenic greenhouse gas which results to 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 the greenhouse effect (Barbalace, 2006). These gases have significant absorption bands in the infrared range, contributing considerably to the increase in greenhouse effect. The life span of greenhouse gases such as carbon dioxide may be up to 200 years (US DoC , 2014). CO_2 is known to be the commonest greenhouse gas emitted into the atmosphere in high amounts (Lim et al., 2013). Carbon dioxide emissions can be minimized in two ways; by reducing the consumption of fossil fuels and move towards technologies not emitting CO_2 or by capturing and storing the CO_2 produced in an attempt to close the carbon cycle. The first solution will require the deployment of alternative renewable energies, or improving the energy efficiency of existing systems. But, the second solution may require the development of carbon capture and sequestration technologies. This study seeks to explore the second option which speculates that CO_2 capture is the best alternative to minimize the emission of CO_2 into the atmosphere. In this context, adsorption technology is envisaged to be a viable technology for CO_2 capture

According to reports from the international panel on climate change , it is estimated that in order to reduce global warming or limit global average temperatures to 2 ^{o}C by 2050, global CO_2 emissions should be reduced by at least 50% (IPCC, 2007). 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 considered to be one of the leading and easiest way of reducing carbon emissions in the atmosphere (Abu-Zahra et al., 2011). Currently, CO_2 capture via adsorption technology have drawn keen attention globally because of the relatively low energy consumption and the high purity CO_2 streams it produces (Serna-Guerrero

and Sayari, 2010). Consequently, variety of adsorbents have been developed and evaluated for such purposes (Choi et al., 2009).

Adsorbents play very important 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). A good adsorbent for CO_2 capture in any industrial application is expected to have a high CO_2 adsorption capacity, 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 understanding of the behaviour of the adsorbent during 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 investigated. In the light of the aforementioned reasons, a new adsorbent called polyaspartamide (PAA) was recently developed and evaluated for CO_2 capture (Ngoy et al., 2014). This adsorbent has proven to be an effective adsorbent for CO_2 capture in terms of its high affinity for CO_2, high adsorption capacity and good thermal stability of about 250^{o}C (Chitsiga et al., 2016). But the behaviour of this adsorbent "polyaspartamide' as regards its adsorption kinetics, rate-limiting step, breakthrough curves and effect of operating parameters on its CO_2 adsorption capacity has not been adequately studied.

The work presented in this dissertation was targeted at investigating the CO_2 adsorption behaviour of polyaspartamide for post-combustion CO_2 capture using modelling and experimental approaches. Mathematical models were used in this study to introduce assumptions and approximations as well as allow for the description of system properties over a wide range of operating conditions which might not easily be solved using real data. The basic prerequisite for developing the models considered in this study was a thorough knowledge of the chemical and physical properties of pure components and mixtures involved in the process. The models were solved and implemented in Matlab environment using MATLAB R2014a (Release 2014).

In a nutshell, this study explored some selected adsorption models and their numerical solutions; each model was fitted into experimental data in MATLAB R2014a and then analysed. Different model parameters were related to the adsorption mechanism and behaviours of the adsorbent. The model that closely fits the experimental data with less percentage error (1.55 %) was further

developed to study the adsorption behaviour of polyaspartamide during post combustion CO_2 capture. An analysis of different operating parameters on the effect of adsorption of CO_2 onto polyaspartamide during post-combustion CO_2 capture was also carried out to pave a way for possible optimization, scale-up and design of an efficient CO_2 capture system using this adsorbent. Theoretical results obtained from the models were validated with experimental data and recommendations for further study were also made.

1.2 Problem statement

Climate change as a result of global warming due to indiscriminate emission of CO_2 into the atmosphere is among the major challenges facing the world today (Chitsiga et al., 2016). In view of this, researchers are working tirelessly to find solution to this global problem. Experiments have been conducted and reported on the application of polyaspartamide (PAA) for post-combustion CO_2 capture (Ngoy et al., 2014); but modelling and simulation of the behaviour of this novel amine-grafted polysuccinimide material during CO_2 capture has not been adequately investigated. Understanding the behaviour of polyaspartamide as an adsorbent for CO_2 capture using modelling and experimental study is very useful in the area of adsorbent design, optimization and scale-up. Polyaspartamide has proven to be a promising adsorbent for CO_2 capture experimentally but its adsorption kinetics under different adsorption conditions is not sufficiently investigated and reported. Flue gas from power plants contains moisture and effect of moisture and other operating variables on polyaspartamide as an adsorbent during CO_2 capture has not been sufficiently investigated and reported as well. Understanding the complete behaviour and performance of this adsorbent for post combustion CO_2 capture is very essential in order to improve its efficiency during CO_2 capture. Mathematical modelling and numerical simulation is a useful tool in understanding the behaviour of many adsorbents in terms of their adsorption capacity and the effects of operating variables during the CO_2 adsorption process (Gani et al., 2002; Shafeeyan et al., 2014). It is therefore imperative to explore mathematical models that will sufficiently predict the CO_2 adsorption capacity of polyaspartamide and also describe its behaviour during post-combustion CO_2 capture under different operating conditions. Parametric effect of moisture, temperature, inlet gas flow rate and operating pressure on the CO_2 adsorption capacity of polyaspartamide during CO_2 capture has not been sufficiently investigated and reported as well. Understanding the complete behaviour and performance of this adsorbent

for post combustion CO_2 capture is very essential in order to improve its efficiency during CO_2 capture. Mathematical modelling and numerical simulation is a useful tool in understanding the behaviour of many adsorbents in terms of their adsorption capacity and the effects of operating variables during the CO_2 adsorption process (Shafeeyan et al., 2014). It is therefore imperative to explore mathematical models that will sufficiently predict the CO_2 adsorption capacity of polyaspartamide and also describe its behaviour during post combustion CO_2 capture under different operating conditions.

In spite of series of laboratory reports on the experimental evaluation of polyaspartamide for CO_2 capture (Ngoy et al., 2014), little or no investigations focused on the modelling and simulation of the CO_2 adsorption behaviour of this adsorbent during post-combustion CO_2 capture towards enhancing the CO_2 adsorption capacity of the adsorbent. In addition, understanding the behaviour of the adsorbent via modelling could pave the way for the design of a good adsorption system to use the adsorbent for CO_2 capture. This dissertation seeks to proffer solutions to the problems highlighted above by exploring models that could be used to describe the behaviour of polyaspartamide during post-combustion CO_2 capture. In addition, the study attempted to simulate the adsorption behaviour of polyaspartamide under different adsorption conditions so as to have an in-depth understanding of its behaviour for future industrial applications in the area of CO_2 capture.

1.3 Justification

Polyaspartamide is an amine rich polymer widely used in drug delivery. However, its rich amine content, porosity and large surface area makes it a very good material that could be considered for CO_2 capture. Hence its behaviour during post-combustion CO_2 capture was investigated in this study using experimental and mathematical modelling approach. Mathematical models are very useful in attempting to fully understand the behaviour of adsorbents in a packed bed adsorption column and also in designing and optimizing any process (Gutiérrez Ortiz et al., 2014). Mathematical modelling approach was applied in this study because models are capable of estimating the breakthrough curve, adsorption kinetics and temperature profile of a certain adsorbent and adsorbate in all locations within the adsorption column. Experimental validation of the model results was also carried out.

Model development has no associated cost as compared with continuous experimentation. More so, previous studies have shown that mathematical models are capable of giving better predictions of the temperature and concentration profiles of the adsorbent among other parameters which describes the behaviour of the adsorbent during the CO_2 adsorption process. Kinetic data of the adsorption of CO_2 onto the adsorbent is another characteristic that is very important for the simulation and design of an efficient CO_2 capture system. This is because, kinetic data significantly influence the residence time required for the completion of any adsorption process as well as the unit capital cost (Serna-Guerrero and Sayari, 2010). In this dissertation, the kinetics of adsorption of CO_2 onto polyaspartamide was investigated using the Lagergren's pseudo 1^{st} and 2^{nd} order and the Avrami kinetic models. The Lagergren's pseudo 1^{st} order and pseudo 2^{nd} order as well as the Avrami kinetic models were considered in this study because they are widely used kinetic models and similar studies on modelling the adsorption of CO_2 on amine-functionalized mesoporous silica (Serna-Guerrero and Sayari, 2010) reported that these kinetic models sufficiently described the adsorption of CO_2 on the amine-functionalized mesoporous silica but the best fit with experimental data was obtained using the Avrami kinetic model. However, this study considered these kinetic models as well in a bid to verify whether the same conclusion applies to the adsorption of CO_2 onto polyaspartamide which is an amine-grafted polysuccinimide. In another similar study, gas-solid adsorption models were applied in the numerical simulation of CO_2 adsorption behaviour on K-based sorbents (Zhang et al., 2016) without looking deep into its kinetics but this study seeks to include the CO_2 adsorption kinetics of polyaspartamide using the same models and also develop a new adsorption model that describes the effect of moisture on the adsorbent under investigation based on the assumptions of the model that closely fit the experimental data during validation. Finally, theoretical results obtained from the models explored in this study were validated with experimental results to confirm whether the model sufficiently described the behaviour of breakthrough curves. The results were compared to that obtained in a similar studies previously carried out (Gupta and Babu, 2009).

1.4 Research Questions

This research seeks to answer the following questions;

1. How effectively can mathematical modelling be used to describe the behaviour and performance of polyaspartamide as an adsorbent for post combustion CO_2 capture?
2. What is the effect of the presence of moisture and other operating variables, such as flow rate, operating pressure and temperature, on the adsorption capacity of polyaspartamide as an adsorbent during post combustion CO_2 capture?
3. What is the effect of diffusion on the CO_2 adsorption behaviour of polyaspartamide?
4. What is the actual mass transfer limitation (rate-limiting step) controlling the adsorption of CO_2 onto polyaspartamide?

1.5 Aims and objectives of the study

The study contained in this dissertation aimed at investigating the behaviour of polyaspartamide during post-combustion CO_2 capture using mathematical models from existing gas-solid adsorption kinetic, diffusion and rate-limiting models and also study a general model that will give sufficient information on the behaviour of the adsorbent as well as investigate the effect of operating variables such as flow rate, pressure and temperature as well as moisture on the CO_2 adsorption capacity of the polyaspartamide during post-combustion CO_2 capture. This study also seeks to come up with a mathematical model that can be used to study the effects of moisture on the adsorption capacity of adsorbents and also recommend a scale up, optimization and design of an adsorption system for post-combustion CO_2 capture using polyaspartamide as an adsorbent.

The following are the specific objectives of this research work;

1) To investigate the behaviour of polyaspartamide as an adsorbent for post combustion CO_2 capture in terms of its kinetics of adsorption, adsorption mechanism, mass transfer limitation etc. via modelling and experimental study approach.
2) To validate the model by reconciling the outcome of the model with results obtained from experiments and then do a numerical simulation in the MATLAB environment.

3) To investigate the effects of operating variables such as operating pressure, flow rate and temperature on the CO_2 adsorption capacity of polyaspartamide during CO_2 capture.

4) To study the effect of the presence moisture on the adsorption capacity of polyaspartamide during post-combustion CO_2 capture.

1.6 Dissertation Outline

Chapter One:

This chapter presents a general introduction to the purpose of the completed work, its motivations as well as aim and objectives.

Chapter Two:

This chapter contains a critical literature review where pertinent literatures on CO_2 capture, mathematical modelling of the behaviour solid adsorbents, numerical simulation, CO_2 adsorption technology in power plants and detailed information concerning polyaspartamide as an emerging adsorbent for carbon dioxide adsorption were extensively reviewed and explained. A published review article on CO_2 capture technologies in coal-fired power plants emanated from this chapter and the full paper has been included in the appendix section of this dissertation.

Chapter Three:

This chapter presents the general experimental layout, materials and methods used in this study. The methods of linearizing the models explored and fitting to experimental data were also discussed in this chapter. This chapter also relates the study to prior work that has been done on this specific adsorbent.

Chapter Four:

In this chapter, existing gas-solid adsorption models as well as three kinetic models with two rate-limiting step models and the Boyd's film diffusion model were explored and the model parameters relating to adsorption mechanism and behaviour of polyaspartamide during post-combustion CO_2 capture in a packed bed adsorption column were solved in MATLAB R2014a.

The respective breakthrough curves, kinetics of adsorption were presented and discussed extensively. Validation of the models with experimental data was also carried out in this chapter. The adsorption behaviour of polyaspartamide as an adsorbent during post-combustion CO_2 capture was extensively investigated and discussed using modelling and experimental approaches. Selected gas-solid adsorption models and kinetic models were also extensively explored in this chapter. This study conducted in this chapter was carried out to achieve the first and second objectives of this study. The content of this chapter has been accepted for publication in a reputable journal.

Chapter Five:

This chapter focused on the diffusion mechanism and the rate-limiting steps controlling the adsorption of CO_2 onto polyaspartamide. Various gas-solid diffusion models were extensively investigated and results were discussed and presented in this chapter. The third objective of this study was achieved in this chapter. A manuscript was written from this chapter and has been submitted for possible publication.

Chapter Six:

This chapter was dedicated to understanding the effect of moisture and other operating parameters such as operating pressure, CO_2 inlet flowrate, and adsorption temperature on the adsorption capacity of polyaspartamide as an adsorbent during post combustion CO_2 capture. The Fourth objective of this study was achieved in this chapter. One manuscript was submitted for publication from this chapter.

Chapter Seven:

This chapter is an extended part of this research. It is a preliminary investigation carried out to study the kinetic behaviour of adsorbents using selected kinetic models. The selected models in this study were tested on a chitosan-impregnated sodalite-zeolite metal organic framework (Sod-ZMOF/Chitosan) which has a polymer backbone similar to polyaspartamide and discussed in this chapter to determine the feasibility of a similar study on polyaspartamide which have close similarity with sod-ZMOF/Chitosan. The assumptions of these models were also clearly defined in this chapter. Apart from the traditional gas-solid adsorption models, diffusion as well as rate-

limiting step models were suggested for the main study in this chapter. This chapter paved way for a successful study on polyaspartamide which is the main study in this research. A conference paper was published from this chapter and attached in the appendix section.

Chapter Eight:

This chapter reported a general summary of the study conducted and overall conclusions from preceding chapters and recommendations for future study were made.

References to all articles consulted in the course of this study are provided at the end of each chapter of this dissertation. An appendix section which provides relevant experimental results, MATLAB codes, other important data as well as the research output of this study in form of publications from this present work is provided at the end of this dissertation.

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CHAPTER TWO

Literature Review

2.0 Introduction

CO_2 capture is widely accepted as an important option to reduce worldwide CO_2 (greenhouse gas) emissions from point sources. CO_2 is one of the major anthropogenic greenhouse gases usually emitted into the atmosphere and as such, using an effective capture route for CO_2 from industrial and commercial operation is essential to the reduction of CO_2 emitted from these sources (Pires et al., 2011). Chemical absorption of CO_2 using monoethanolamine (MEA) is currently a widely used technology for CO_2 capture (Abdeen et al., 2016). It is regarded as a mature technology for CO_2 capture because of its wide industrial applications. However, the absorption technology using monoethanolamine comes with some demerits such as high energy demand during solvent regeneration and environmental issues due to the degradation of monoethanolamine. Physical adsorption of CO_2 using solid adsorbents is currently attracting attention as an alternative technology for CO_2 capture due to its competitive advantages over the absorption technology (Burghaus, 2014). In the adsorption technology, adsorbents play a very important role because recent studies on the capture of CO_2 from flue gas streams focus on the development as well as performance evaluation of adsorbents for CO_2 capture.

In addition, holistic understanding of the behaviour of the developed adsorbents is paramount to designing an adsorption process for the material. Mathematical modelling is a very useful tool to do this. Mathematical modelling of adsorption processes play an increasingly important role in CO_2 capture studies. Such models are typically needed for various tasks including process design, process analysis and optimization of process conditions, as well as for model-based control (Daramola et al., 2011). Therefore, application of mathematical models to understand the behaviour of adsorbents for CO_2 capture is considered to be a useful tool.

Over the past decades, mathematical models have become widely applied in a broad range of chemical engineering activities, such as product and process design and development, process monitoring and control, real time optimization of plant operation or supply chain management (Daramola and Okosun, 2015). In addition, research has shown that mathematical modelling of

chemical and biochemical processes plays an increasing role in today's competitive industries, and such models are typically needed for various tasks including process design, process analysis and optimization of process conditions, material design as well as for model-based control (Marriott et al., 2001; Daramola et al., 2008).

Koronaki et al (2015) presented the modelling of CO_2 capture via the adsorption technology using a rate-based and dynamic modelling approach. They concluded that adsorbents play an important role in the adsorption process. Enaasen-Flø et al. (2015) developed a dynamic model to validate the adsorption of CO_2 using amines, scanty reports have been made as regards the absorbents and their kinetic behaviour. Post-combustion CO_2 capture using solid adsorbents was reviewed by Samanta et al (2012) where the desired attributes of solid adsorbents like metal organic frameworks, zeolites, carbon nanotubes, activated carbon, carbon molecular sieves were assessed in terms of various desired attributes such as adsorption capacity, selectivity, regeneration etc. The authors concluded that solid sorbents are promising alternatives for CO_2 capture because of their non-toxic nature and very fast kinetics.

In this chapter, a critical review of literature on CCS, numerical simulation and mathematical modelling on gas-solid adsorption process is presented.

2.1 CO_2 Emission

CO_2 among other greenhouse gases is the largest contributor to global warming (Anderson et al., 2016). Power generation, cement production and the use of fossil fuels have resulted in the emission of high amounts of CO_2 into the atmosphere over the past decades. About 321 billion tons of CO_2 have been emitted into the atmosphere from 1951 till date and a larger part of these emissions happened in the mid-1970s (Ming et al., 2014). Between 1970 and 2002, global emission of CO_2 has increased by over 70% (Alhorr et al., 2014). There have been great concerns over the increase in the atmospheric concentration of CO_2 and its hard effect on the environment which prompted various efforts around the globe on how to capture CO_2 from point sources and stabilize the high concentration of CO_2 in the atmosphere (Singer et al., 2014). Emissions of CO_2 from power plants that use fossil fuels like coal and natural gas are the most important sources of CO_2 emission into the atmosphere (Turnbull et al., 2016), therefore it is

necessary to recover and capture CO_2 from these sources in order to reduce the high concentration of CO_2 being emitted into the atmosphere.

There are greater natural sources of CO_2 emissions than there are sources of CO_2 emission due to human activities (anthropogenic CO_2) (Surugiu et al., 2012). Natural sources of CO_2 are closely balanced by naturally occurring phenomena such as photosynthesis and weathering of rocks. This balance has made the atmospheric concentration of CO_2 to be as low as 260-280 ppmv for 10,000 years before the start of the industrial era (Schubert and Jahren, 2012; Liu et al., 2015). During the industrial era, the demand for electricity was on the increase and power generation in turn accounted for almost 50% increase from beginning of year 2000 (Luo et al., 2015; Shim and Hong, 2016). The global fossil fuel CO_2 emission estimate also rose to about 25000 metric tons in 2002. There is a growing energy demand globally and it is expected to increase by over two-third by 2030. Fossil fuels will still remain the primary source of energy which will be on the increase by over 90% (Popp et al., 2014; He, 2015). Sources of CO_2 emissions are presented in Table 2.1 while the percentage of capturable and uncapturable anthropogenic CO_2 is presented in Figure 2.1.

Table 2.1 Sources of CO_2 emissions in South Africa (Adapted from: Varga, 2013; Al-Salem, 2015; Hermawan et al., 2015)

Source of Likely Capturable CO_2	Amount of CO_2 (Mt/a)
Electricity generation	137
Process industries	24
Other energy production companies	26
Manufacturing companies	26
Municipal wastes	9
Agricultural wastes	41
Other wastes	36
Thermal energy production	32

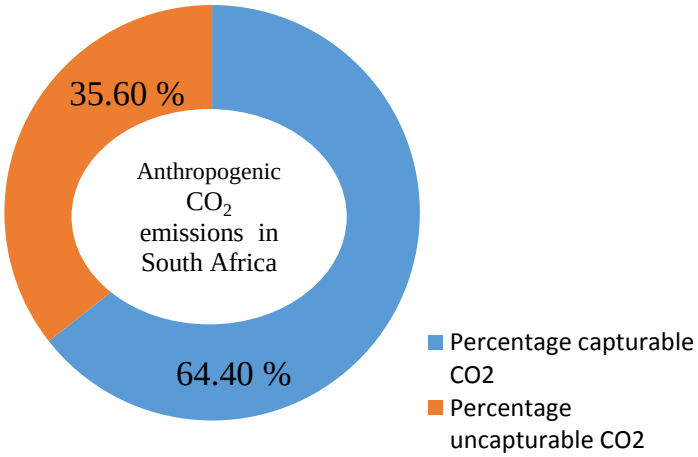


Figure 2.1 Percentage of capturable and Uncapturable CO_2 (Adapted from Yoro and Sekoai, 2016)

2.2 CO_2 Capture and Storage (CCS)

Basically, the concept of CO_2 capture and storage is to reduce the emission of anthropogenic CO_2. Carbon dioxide capture entails trapping CO_2 generated from large point sources and compressing it for easy transportation to storage or utilization sites. CCS is a comprehensive technology for the direct reduction of the CO_2 emission into the atmosphere. In this study, investigation of a CO_2 capture system using a solid sorbent was undertaken.

2.3 CO_2 Capture in Coal-Fired Power Plants

The integration of clean and sustainable energy technologies in the energy sector requires solutions that deal with high CO_2-emitting sources, such as coal-fired power plants (Boudri et al., 2002). This implies that sustainability assessment of CCS technology is an important aspect of climate policy, especially in highly industrialized countries (Khoo et al., 2011). However, CCS has some technical and economic barriers that should be addressed before it can be implemented on the industrial scale. CCS is hindered by economic, social and legal barriers (Lilliestam et al., 2012). In addition, there are limited geological storage capacity for CO_2 capture in some countries; thereby making CO_2 storage a mirage (Figueroa et al., 2008).

In South Africa, power generation from the combustion of fossil fuel (coal) is the major source of anthropogenic CO_2 into the atmosphere. Carbon capture and storage (CCS) from coal-fired

power plants is attracting increasing attention as an alternative approach towards the reduction of carbon dioxide emission. Therefore, innovative strategies and process optimization of CCS systems is essential in order to improve the process efficiency of this technology in South Africa.

The development of CCS is still in its infancy in most developing countries today, implying that there are no frameworks for this technology in most countries (Zheng and Xu, 2014). Against this background, this chapter examines the potential of CCS technology via adsorption technology in mitigating CO_2 emitted from coal-fired power plants. It investigates the various CCS methods that could be applied to capture the CO_2 generated from these coal-fired power plants. Lastly, it recommends the use of new adsorbents that could be utilized towards the implementation of CCS systems in coal-fired power plants and also the retrofitting of capture devices into the existing coal-fired power plants. This study also examined the behaviour of a novel polymer-based adsorbent (polyaspartamide) with a view to upscale, optimize and prepare it for future industrial or pilot-scale industrial application in the area of CO_2 capture.

2.4 Technological Routes for CO_2 Capture

The generation of CO_2 is inherent in the combustion of hydrocarbon fuels, which is a daily occurrence in coal-fired power plants (Bui et al., 2014; Cebrucean et al., 2014; Gaspar et al., 2016). Currently, pre-combustion, post-combustion and oxy-fuel combustion captures are the three basic technological routes used to capture CO_2 (Khalilpour, 2014; Enaasen Flø et al., 2015; Flø et al., 2016). These technological routes for CO_2 capture and their possible implementation in coal-fired power plants are discussed in this section.

2.4.1. Post-Combustion CO_2 Capture

Post-combustion CO_2 capture involves the capture of CO_2 from flue gas streams after the generation of electricity (Favre, 2007; Wall, 2007; Åkesson et al., 2012). This method is very effective for capturing CO_2 from power plants. It is also known as post-conversion capture, but when applied in power plants, it is referred to as post-combustion capture (Calvo-Muñoz et al., 2016). The technologies deployable in post-combustion CO_2 capture include solvent absorption, solid sorbent adsorption, membranes and cryogenic separation (Schakel et al., 2014; Otto et al., 2015;). Out of all of these options, CO_2 capture via absorption using monoethanolamine is

extensively used and referred to as a very mature technology (Singh et al., 2011). Post-combustion capture is still considered as the most mature capture route because it is widely embraced in many industrial applications with better operational flexibility (Mason et al., 2011; Román, 2011; Lee et al., 2012; Gilassi and Rahmanian, 2015). Post-combustion CO_2 capture is widely used during power generation because it has the possibility of retrofitting capture systems into existing power plants. The schematic for post-combustion CO_2 capture is depicted in Figure 2.2.

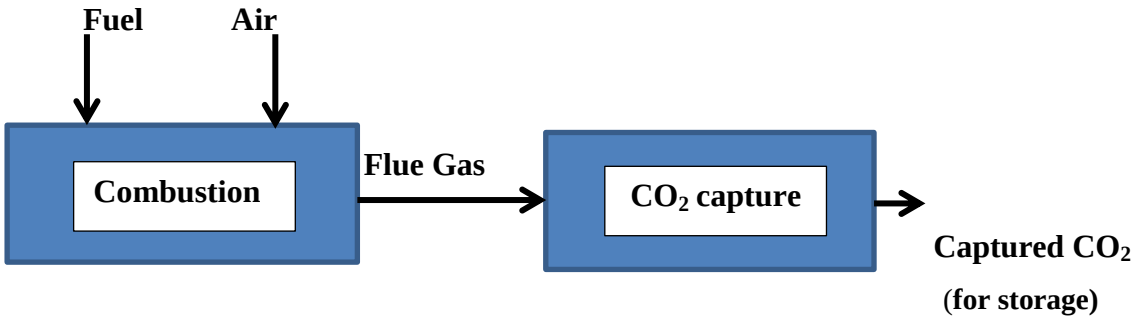


Figure 2.2 Post-combustion CO_2 capture

The world's energy sector is mainly driven by the combustion of fossil fuels, and the sustainable use of fossil fuels in these power plants must continue in order to avoid energy crisis. On this note, retrofitting CO_2 capture systems in the already existing coal-fired power plants becomes a viable option in order to reduce CO_2 emission into the atmosphere. Since the post-combustion technology allows for possible retrofitting, it becomes a promising technology that can be implemented in coal-fired power plants. The major disadvantage of retrofitting these CO_2 capture devices into existing power plants is that there will be a slight reduction in plant efficiency; leading to an increase in cost of power.

2.4.2 Pre-Combustion CO_2 Capture

The pre-combustion capture refers to the capturing of CO_2 generated as an undesired co-product of a conversion process (Liu et al., 2015; Cuéllar-Franca and Azapagic, 2015; Kumar et al., 2016). In pre-combustion CO_2 capture, coal is gasified using oxygen/air (Rao and Rubin, 2002; Davison, 2007; Tontiwachwuthikul et al., 2011; Singto et al., 2016;). Syngas produced from the gasification process is then steam-reformed to CO_2 and H_2 via water-gas shift reaction (WGS). The produced CO_2 is finally separated using a physical or chemical absorption process (Sema et

al., 2013; Xu et al., 2014). Physical solvents are most suitable for use at high operating pressure and low temperatures (Bhown and Freeman, 2011; Songolzadeh et al., 2014).. A schematic representing pre-combustion CO_2 capture is shown in Figure 2.3.

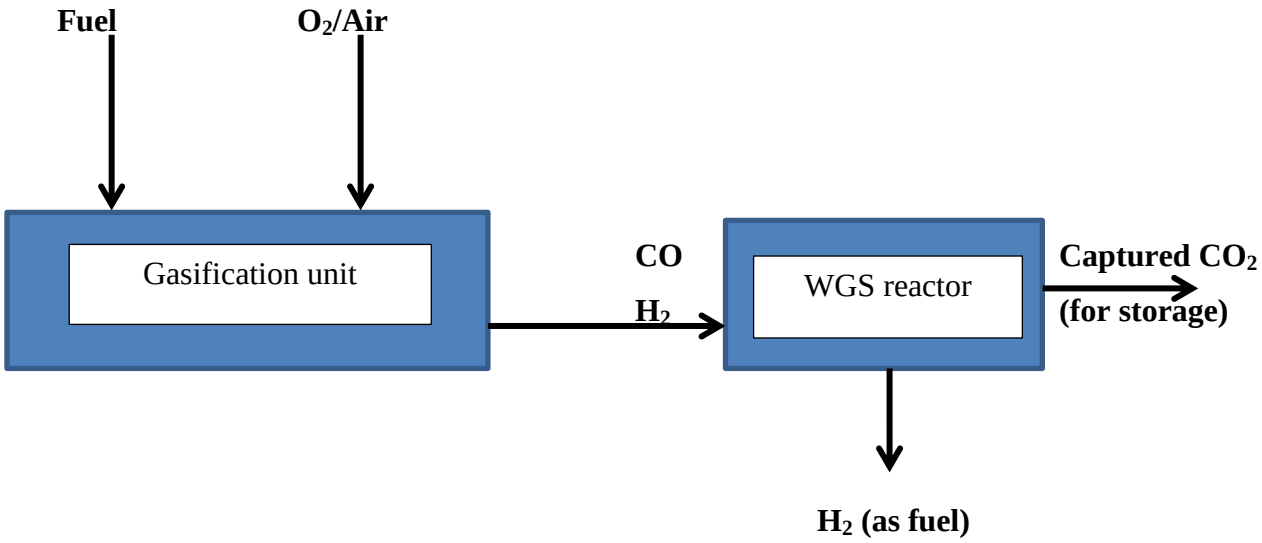


Figure 2.3 Schematic representation of the pre-combustion CO_2 capture process

In a typical pre-combustion setup, the fuel (coal) is partially oxidized with oxygen (O_2), air or steam to liberate carbon monoxide (CO) and hydrogen (H_2) in a chemical process known as reforming. A further shift reaction of carbon monoxide and hydrogen liberates carbon dioxide (CO_2) and hydrogen (H_2). This takes place in a water gas shift (WGS) reactor where the CO_2/H_2 gas mixtures can be separated into individual components. The H_2 produced can serve as fuel in a gas turbine combined cycle plant. This technology is mostly used in integrated gasification combined cycle (IGCC) for coal gasification. The CO_2 concentration in the IGCC is in the range of 35 % – 40 % (vol/vol) with a total pressure of about 20 bar or more in the stream leaving the IGCC (Olajire, 2010).

2.4.3 Oxy-Fuel Combustion CO_2 Capture

In the oxy-fuel combustion technological approach for CO_2 capture, the fuel is burnt in the presence of pure oxygen instead of air. The oxy-fuel combustion CO_2 capture produces a flue gas stream that is highly concentrated with CO_2 (Uchida et al., 2013; Stanger et al., 2015). This technology also produces flame with an excessively high temperature; because theoretically, if fossil fuel is burnt in pure oxygen, much heat is produced (Aaron and Tsouris, 2005;

Babamohammadi et al., 2015). The pure oxygen is produced by cryogenics or membrane separation of oxygen from air. The main advantage of the oxy-fuel CO_2 capture technique is that the flue gas is available at a high CO_2 concentration thereby reducing separation costs (Yan et al., 2011; Borgert and Rubin, 2013). This is due to the fact that oxy-fuel combustion uses pure oxygen instead of air which eliminates N_2 from the flue gas stream. Although this technology appears promising if implemented for CO_2 capture in power plants, its implementation in the coal-fired power plants of most developing countries is quite slim because burning coal in pure oxygen instead of air on a large scale is very expensive (Yoro and Sekoai, 2016). This will in turn increase the cost of electricity. Therefore, it is not an economically suitable technological route for CO_2 capture in power plants. Another major problem associated with this technology is the huge cost involved in the separation of O_2 from air. A schematic for the oxy-fuel combustion capture route is presented in Figure 2.4.

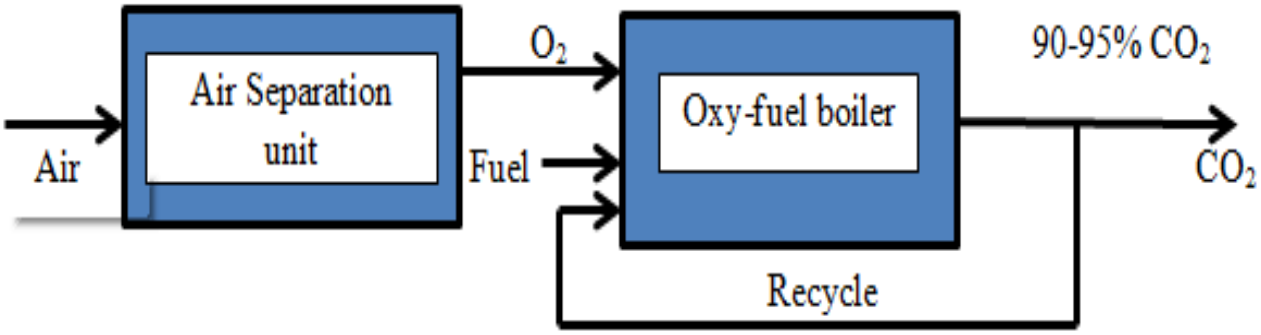


Figure 2.4 Oxy-fuel combustion capture.

2.5 Separation Technologies for Post-Combustion CO_2 Capture

The preference of one technological route over the others could be attributed to its ease of access, possibility of implementing the capture process, ease of retrofitting to existing power plants, the maturity level of such a technological route and the period needed for the implementation of such technology (Olajire, 2010). Currently, there is a wide range of CO_2 capture and separation techniques from gas streams, which could be implemented in coal-fired power plants (Yang et al., 2011). They are based on physical and chemical processes, which include adsorption, absorption, cryogenic and membrane separation technologies. They are shown in Figure 2.5 and also discussed below:

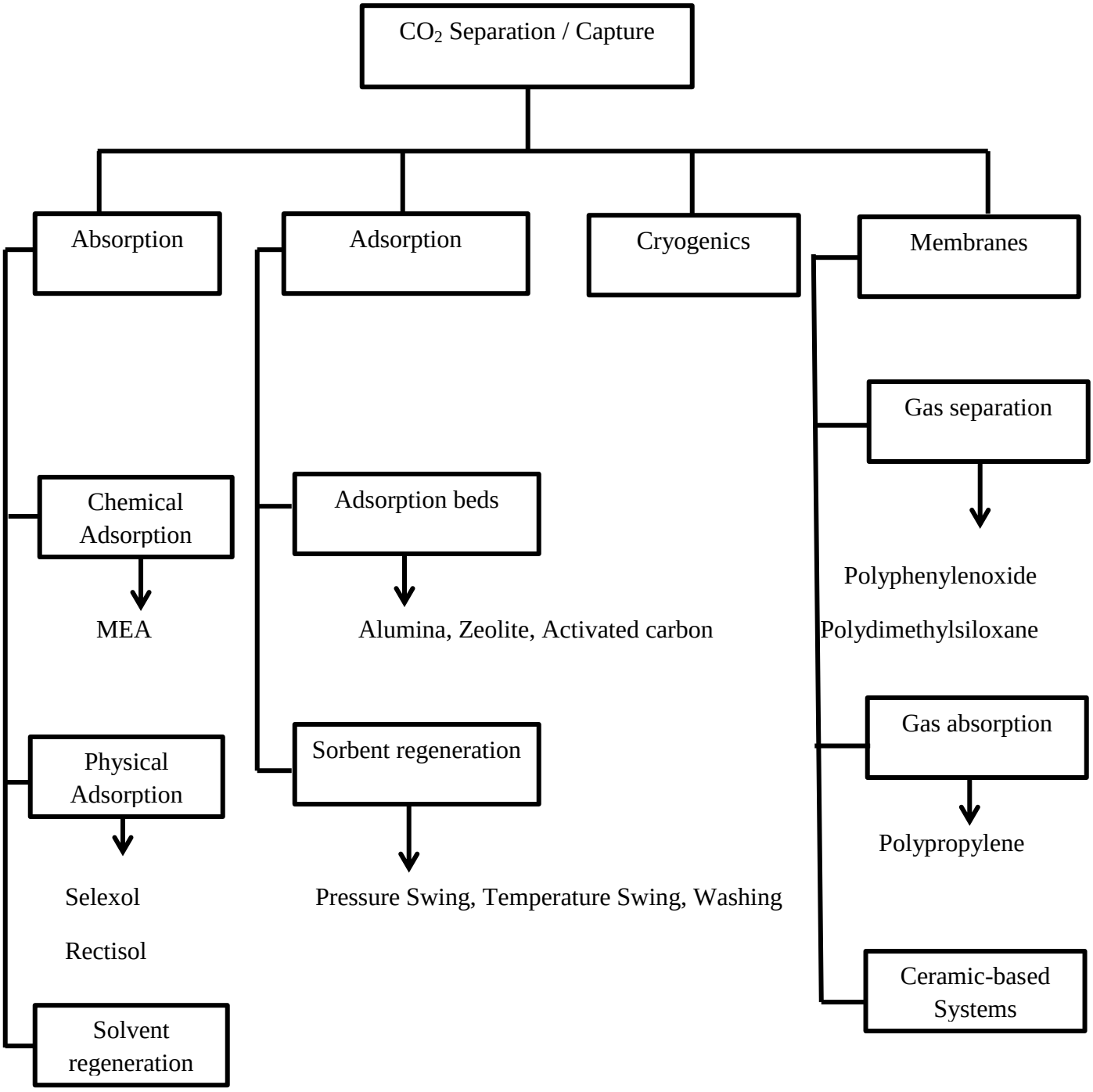


Figure 2.5 Different CO_2 separation and capture technologies for post-combustion CO_2 capture (Adapted from: Siriwardane et al., 2001).

2.5.1 Cryogenic Separation

The cryogenic separation of CO_2 is mainly based on the principle of condensation and cooling (Belaissaoui et al., 2012; Li et al., 2014). It is mostly applied in CO_2 capture systems where the gas streams contain a high concentration of CO_2. The challenge about cryogenic separation is that most power plants have a more dilute CO_2 stream (Fu et al., 2016; Scholes et al., 2016). Another setback is that this technology is energy intensive, i.e., it requires high amounts of energy for CO_2 separation. Since the concentration of CO_2 from most coal-fired power plants is quite low depending on the combustion method used, this CO_2 separation method appears difficult to implement. Furthermore, cryogenic separation is best carried out at very low temperatures (Kansha et al., 2011). However, it is difficult to attain very low temperatures in coal-fired power plants that will be suitable for CO_2 capture using this technique. In most cryogenic separation processes, various components in gas mixtures are separated by a series of compression, refrigeration and separation steps (Fu et al., 2014). Impurities lower the phase transition temperature of CO_2 in cryogenic separation processes to as low as −80 °C. In this case, the refrigeration energy penalty increases substantially, and there is a huge possibility of CO_2 frost formation, which is a threat to equipment safety (Khalel et al., 2013).

2.5.2 Membrane Separation

Corti and Lombardi (2004) investigated CO_2 capture using membranes and concluded that the application of CO_2 capture from flue gases using membranes can only be competitive if the CO_2 concentration in the flue gas is higher than 10%. CO_2 capture using membranes operate on the principle of differences in the physical or chemical interaction between the CO_2 gas and the membrane. The membrane is designed in such a way as to allow one gas pass through faster than the other (Bandyopadhyay, 2011). Compared to existing technologies like absorption and adsorption, CO_2 capture using membranes possess some clear advantages over absorption and adsorption processes, this is because, they have simple modular systems, no waste streams and no energy is required during regeneration. Limitations of conventional gas absorption towers and adsorption processes is eliminated in membrane separation, thus offering high selectivity and high driving force with a simple modular design (Aoki et al. 2000; Li et al., 2014; Scholes et al., 2014). Although the membrane technology is relatively new, it is widely known for its high selectivity as compared to other conventional methods (Yan et al., 2008; Brunetti et al., 2010). In

addition, this technology uses either inorganic ceramic membranes or organic polymeric membranes (Stanislowski et al., 2013; Tomioka et al., 2013). Ceramic membranes are quite expensive; however, it is very difficult to achieve a high degree of separation of CO_2 and a high purity of CO_2 at the same time with CO_2 in the flue gas through a single-stage ceramic or polymeric membrane. This is a major limitation of this CO_2 capture technology. Polymeric membranes have been extensively studied for CO_2 capture, these membranes are prone to degradation in harsh conditions; which makes them unsuitable for CO_2 capture from flue gas with contaminants like Sulphur (IV) oxide and water vapour (Kazemimoghadam and Mohammadi 2005; Chung et al. 2007; Olajire 2010; Daramola et al, 2015). However, zeolite based membrane technology provides CCS with great number of potentials such as chemical inertness and high thermal stability

Membrane technology is not suitable for post-combustion CO_2 capture. Although the polymeric membranes have excellent selectivity and permeability for CO_2 capture, they have very low thermal stability and these membranes may be plasticized with the influence of CO_2 in the membrane. Therefore, application of the membrane technology for post-combustion CO_2 capture in coal-fired thermal power plants is limited. Efficient capture technologies for CO_2 with low cost and high CO_2 capture potential, as well as selectivity need to be studied further as an alternative to the use of membranes for post-combustion CO_2 capture (Wang et al., 2014).

2.5.3 Absorption

The absorption technology involves the use of chemical solvents to capture CO_2. It is a well-researched, robust and mature technology that is widely applied industrially (Wang et al., 2011; Corsten et al., 2013; Lv et al., 2015). The commonly-used solvents for absorption of CO_2 from flue gases are basically amines (Dave et al., 2009; Richner, 2013), chilled methanol (Pérez-Fortes et al., 2014) and ammonia solution (Kozak et al., 2009; Bonalumi et al., 2016). Although the absorption technology is considered as a mature technology for CO_2 capture, the use of solvents makes it corrosive and energy intensive due to high energy demands during solvent regeneration. The major limitation of this technique is that it uses liquid absorbents, which corrodes pipes in power plants (Aronu et al., 2009; Zhao et al., 2011). Liquids, such as monoethanolamine, react readily with CO_2, but because heat must be applied to remove CO_2 from the resulting liquid, the process is not economically viable for implementation in power

plants. If the approach were applied to every power station in most developing countries, CO_2 capture could cost 30% of each country's growth in gross domestic product each year (Svendsen et al., 2011). Less expensive methods for capturing CO_2 and hydrocarbon emissions with minimal energy costs need to be investigated.

In order to reduce the high thermal energy consumption in the power plants, the concentration of monoethanolamine used during the post-combustion CO_2 capture process should be increased, and better corrosion inhibitors should be used to eliminate the high corrosive effect of monoethanolamine as a solvent for the CO_2 capture by absorption (Tunnat et al., 2014).

2.5.4 Adsorption

This technology is extensively used in chemical and environmental processes. It uses various adsorbents such as zeolites, activated carbon, polyaspartamide, metal oxides; porous silicates, metal organic frameworks and chitosan for CO_2 capture (Ben-Mansour et al., 2016). However, CO_2 capture by adsorption using activated carbon fibres and a carbon fibre component is regarded as an efficient approach when used in power plants (Tseng et al., 2015). Adsorption technology is attracting increasing attention due to its characteristics, which include minimum energy requirements, easy maintenance, simple operation and flexibility (Chen and Lu, 2015). The adsorption technology that uses solid adsorbents for CO_2 capture is highly recommended for use in coal-fired power plants because it is not corrosive, it is least expensive and has minimum energy requirements for the regeneration of the solid adsorbents (Luis, 2016). Amongst the adsorption processes reported in literature, temperature swing adsorption (TSA) is an advantageous process because it is inexpensive and uses less thermal energy. Therefore, it can reduce the operating costs if it is incorporated into coal-fired plants (Darunte et al., 2016; Yan et al., 2016). However, it requires longer cooling and heating times for CO_2 capture (Saxena et al., 2014). Meanwhile, vacuum swing adsorption (VSA) is more economically viable than pressure swing adsorption (PSA) in post-combustion for CO_2 capture (Yang et al., 2014). Nevertheless, it has its own drawbacks, such as its sensitivity to feed gas temperature. More heat treatment might be needed to condition the flue gas before injecting it to the VSA plant; this affects the separation efficiency and process economics. PSA has been shown to be a promising technology in recent years because it can use a wide range of temperatures and pressures and requires minimum energy. Another advantage is that it requires low investment costs (Freeman et al.,

2014). The adsorption technology also has its disadvantages, such as poor heat transfer, especially in packed-bed columns, and slow kinetics, but the advantages of this technology far out-weigh its disadvantages (Leung et al., 2014). There is potential in the implementation of this technology in most power plants because of its ease of regeneration of the adsorbent using pressure modulation with reduced energy requirements.

2.6 CO_2 Storage

When CO_2 is successfully captured from these coal-fired power plants, it can be stored in natural areas, like geological formations, where it is trapped below impermeable rocks and retained in pore spaces after being dissolved by underground water (Little and Jackson, 2010; Verdon, 2014). This method of storing CO_2 has a long residence time. This means that CO_2 can also be stored in geological formations, such as unused deep saline aquifers. According to literature reports, the geological storage of CO_2 is currently considered as the most viable option for storing captured CO_2 in large quantities (Michael et al., 2010; Czernichowski-Lauriol and Stead, 2014). Geological storage formations can store up to 10 million tons of CO_2 for a long period of time (Aydin et al., 2010). However, good geological sites for CO_2 storage must have: (i) appropriate thickness and porosity; (ii) the reservoir rock must be permeable and (iii) the cap-rock must be in a stable geological environment, as well as having a good sealing capability. Depleted or almost depleted oil and gas reservoirs, saline aquifers and un-mineable coal beds are the three major geological formations commonly considered for CO_2 storage (Suekane et al., 2008; Streimikiene and Mikalauskiene, 2010). Storing CO_2 in deep oceans is another option for CO_2 storage; however, it poses environmental concerns, such as eutrophication and ocean acidification. Captured CO_2 could be stored in oceans by releasing it into deep ocean waters of a minimum depth of 1000 m below sea level. This form of CO_2 storage is feasible because cold-deep sea waters are unsaturated with CO_2 and subsequently have a significant potential of dissolving it. This is based on the principle that CO_2 becomes super critical below certain depths with a liquid-like density; and also, it is less buoyant than water (Qanbari et al., 2011; Klapperich et al., 2014). However, as stated earlier, the major disadvantages of this option are the environmental challenges attributed to it.

The most suitable option of storing the captured CO_2 from coal-fired power plants is by using geological formations, like deep saline aquifers at 700–1000 m below ground level. Carbon

dioxide is soluble in water; there are natural exchanges of CO_2 between the atmosphere and waters at the ocean surface that occur until equilibrium is reached. If the atmospheric concentration of CO_2 increases, the ocean gradually takes up additional CO_2. In this way, the oceans have absorbed about 500 Gt CO_2 of the total 1300 Gt CO_2 of anthropogenic emissions released to the atmosphere over the past 200 years (Gershenzon et al., 2014). As a result of the increased atmospheric CO_2 concentrations from human activities relative to pre-industrial levels, the oceans are currently absorbing CO_2 at a rate of 7 Gt CO_2 per year. Most of this carbon dioxide now reside in the upper ocean and thus far, has resulted in a decrease in pH of about 0.1 at the ocean surface because of the acidic nature of CO_2 in water. To date, there has been virtually no change in pH in the deep ocean. Models predict that over the next several centuries, the oceans will eventually take up most of the CO_2 released to the atmosphere as CO_2 is dissolved at the ocean surface and subsequently mixed with deep ocean waters (Barry et al., 2004).

2.7 An Overview of CO_2 Capture Using Solid Sorbents

CO_2 emissions from coal-fired power plants can be captured using solid sorbents (Krutka et al., 2013). Even though it is less mature than the absorption method, it is inexpensive; it has minimum energy requirements and uses non-corrosive materials (Gibson et al., 2016). Adsorption of CO_2 can be achieved by using various solid support systems, such as activated carbon, zeolites, carbon molecular sieves and polymeric adsorbents like amine-grafted polyaspartamide (Li et al., 2016; Yoro and Sekoai, 2016). According to Chaffee et al. (2007), physical adsorption of CO_2 using solid adsorbents require less energy as compared to other CO_2 capture systems. Physical adsorption of CO_2 requires about 0.09 KWh/kg CO_2 with equal pressure in the feed and product streams, which is by far smaller than the chemical adsorption, which requires about 0.34 KWh/kg CO_2. Yang et al. (2008) conducted a study on modelling the physical adsorption of CO_2 using solid physical adsorbents and investigated CO_2 capture via the pressure swing adsorption methods using activated carbon, zeolite13X, and concluded that the adsorption technology is less expensive and less energy intensive for capturing CO_2. Similar findings with the use of molecular sieves and activated carbon were also confirmed by Othman et al (2009). Rivas and Prausnitz. (1979) indicated that solid adsorbents are more efficient than liquid systems. For example, solid adsorbents exhibit better performance at partial pressures

greater than 50 kPa of CO_2 (Berger and Bhown, 2013; Ruiz et al., 2013; Morris et al., 2014). However, liquid absorbents stabilize when coupled to chemical absorbents. Since the adsorption of gases is favoured by higher pressures and lower temperatures, CO_2 capture from these power plants need to be carried out at high pressures; therefore, the adsorption technology will be ideal for effective CO_2 capture.

Physical adsorbents have also been proven to capture CO_2; they have a high affinity for CO_2. However, the purity of the gas decreases during the downstream process (Nelson et al., 2014). It was indicated that activated carbon and polymer-based adsorbents are the best type of physical adsorbents to be used for CO_2 capture. They produce about a 75–80% pure CO_2 stream at a recovery of 90% (Gray et al., 2008). Adsorption systems do not use high energy, and the recovery is far less than the chemical absorption methods (Glier and Rubin, 2013). Furthermore, polymer adsorption systems have been shown to bind CO_2. A study conducted by Diaf and Beckman, (1995) assessed the effects of polymers on CO_2 capture using primary, secondary and tertiary amine-based polymers and concluded that CO_2 binds strongly on basic amines and proposed ethylene diamine (EDA) as the most efficient amine compound for polymer systems. Similar findings were also confirmed by Seçkin et al. (1997), the authors used 1, 4, 5, 6-tetrahydropyrimidine polymer compound to capture CO_2 and concluded that this method was more feasible compared to other CO_2 capture methods. The effectiveness of CO_2 binding was attributed to the 1:1 nature of amidine groups in the 1, 4, 5, 6-tetrahydropyrimidine (Seçkin et al., 1997). These findings could pave way for the use of carbon dioxide capture technologies via amidine systems (Choi et al., 2011). Studies on modelling of the adsorption behaviour of Sod-ZMOF/Chitosan material during CO_2 capture was presented by Yoro, et al. (2016). The authors concluded that Sod-ZMOF chitosan is a promising adsorbent for CO_2 capture because it exhibited fast kinetics and high adsorption capacity. However, the authors did not consider the diffusion mechanism and rate-controlling steps in their study. Recently, a novel polymer-based adsorbent "polyaspartamide" from polysuccinimide was identified as a promising adsorbent for CO_2 capture because of its ability to selectively adsorb gases; this is due to its molecular sieving characteristics (Ngoy et al., 2014; Chitsiga et al., 2016). The adsorbent was investigated in this study in order to address the limitations of conventional wet solvent processes for CO_2 capture at the pilot scale, such as high costs, high energy requirements and the generation of large quantities of water and sludge from the process (Barzagli et al., 2014). The application of

adsorption technology for CO_2 capture using amine-grafted polymer-based adsorbents is highly encouraged because it is a dry process and has fewer challenges as compared to the conventional process, which uses solvents for CO_2 capture. Against this background, this study investigated the adsorption behaviour of polyaspartamide as an adsorbent for CO_2 capture.

2.7.1 Polyaspartamide as an adsorbent for CO_2 Capture

Before designing an adsorption process, selecting an appropriate adsorbent with high selectivity and adsorption capacity as well as a strong desorption capability is key for post combustion CO_2 capture. In view of this, variety of adsorbents such as synthetic zeolites, activated carbon, carbon molecular sieves, silica and metal oxides have been developed and studied for post combustion CO_2 capture (Shafeeyan et al., 2014). Adsorbents play a key role in adsorption technology. The adsorbent determines the overall CO_2 capture performance in VSA technology (Chaffee et al., 2007). According to Yang et al.(2014), the key elements for a good adsorbent in CO_2 capture technology are;

- High selectivity of CO_2
- High adsorption capacity of CO_2,
- Rapid adsorption/desorption kinetics,
- Stable adsorption capacity after repeated cycles
- Adequate mechanical strength of the particles.

Many adsorbents with high CO_2 adsorption capacity and selectivity such as MOFs, amine modified adsorbents, polymer-based adsorbents have been developed (Plaza et al., 2009; Wang et al., 2010). Polyaspartamide has been studied as a potential adsorbent for post-combustion CO_2 capture (Ngoy et al., 2014). Polyaspartamide (PAA) is an amine grafted polymer-based adsorbent obtained when polysuccinimide reacts with Ethylene diamine (EDA) according to the following equation;

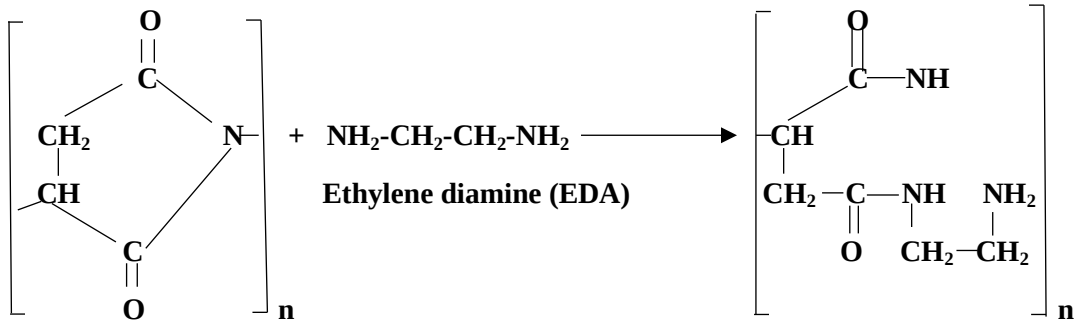


Figure 2.6 Formation of polyaspartamide (Miyata et al., 2008)

Polyaspartamide is considered as a potentially good adsorbent for post-combustion CO_2 capture because of its following properties;

- Large surface area
- Non-toxic nature
- It is biodegradable
- It has good geometry
- It is porous and has high thermal stability.

Chitsiga et al. (2016) improved the adsorption properties of polyaspartamide by freeze-drying the adsorbent which resulted in an improved physical and chemical composition as well as micro-structure. During freeze-drying, mass as well as heat energy was transferred simultaneously through the adsorbent to improve its physical and chemical composition (He et al., 2014; Sehaqui et al., 2015). Adsorbents that are freeze-dried display a spongy and very porous structure which is a desired attribute for the CO_2 adsorption process (Gebald et al., 2011). Hence a freeze-dried amine-rich polyaspartamide was considered in this study. Chitsiga et al. (2016) also investigated the adsorption capacity of polyaspartamide in a thermogravimetric analyser (TGA) using a 100% CO_2 under the following operating conditions; temperature 40^{o}C, pressure 1.1 bar, and flow rate of 60 ml/min and obtained the highest adsorption capacity of 44 gCO_2/kg adsorbent. Using a 100% CO_2 was imperative in order to evaluate the performance of polyaspartamide with pure CO_2 before introducing impurities. This study aims to study the adsorption capacity of polyaspartamide in a packed bed adsorption column where the flue gas is in direct contact with the adsorbent. It is expected that the adsorption capacity of

polyaspartamide will be higher if the experiment was conducted in a packed bed adsorption column because of the direct CO_2-PAA contact. More so, the behaviour and performance of polyaspartamide as an adsorbent was assessed in terms of various desired attributes, such as its equilibrium adsorption capacity, its pore/film diffusion as well as rate-limiting steps, adsorption kinetics, and resistance to moisture. Kinetic and diffusion models were explored in this study to effectively assess the behaviour and performance of this adsorbent during post combustion CO_2 capture.

2.7.2 Regeneration of Polyaspartamide

In every CO_2 capture process, regeneration of the adsorbent is always an integral part. The removal of CO_2 gas molecules adsorbed on to the polyaspartamide adsorbent is hereby discussed. Regeneration of this adsorbent can be studied based on the temperature swing adsorption, vacuum swing adsorption and pressure swing adsorption. When the CO_2 adsorption process comes to an end, the polyaspartamide material gets saturated at breakthrough time. The adsorbent has to be regenerated for re-use. Due to the good thermal stability of polyaspartamide and its stability at very high pressures, the thermal swing and pressure swing desorption could be considered. A possible reason for the higher thermal stability seen in polyaspartamide is that the polymeric fibres of polyaspartamide are linked to one another by resin binders which create a continuous path of conduction through the adsorbent.

During thermal swing desorption in the system, desorption takes place if the temperature of the polyaspartamide material in the adsorption system is raised. The temperature can be raised by exposing the polyaspartamide material to an external source of heat. There is usually a delay between desorption and temperature rise in the adsorbent. However, it is economically viable to stop the regeneration process after the first stage of desorption before the temperature of the adsorbent increases significantly. This helps to reduce the time needed for the adsorbent to be brought to the ambient temperature before starting the CO_2 adsorption process again. Although thermal swing desorption approach helps to reduce cycle time, it could also have significant impact on the adsorption capacity of the adsorbent (Brilman and Veneman, 2013).

Alternatively, the vacuum swing desorption technique can also be considered for the desorption process for this adsorbent. Vacuum swing desorption is considered a promising desorption

option for gases because only the vessel containing the adsorbent is evacuated during the process and not the flue gas as seen in the pressure swing desorption process (Miyata et al., 2008). The associated energy penalty of the vacuum swing desorption is substantially lesser than that of the pressure swing desorption (He and Hägg, 2014). Studies have shown that desorption is increased by over 20% using the electrical swing adsorption method as against the vacuum swing method (Grande et al., 2009; Stern et al., 2013) but the electrical method of desorption was not discussed in this section because the polyaspartamide adsorbent was not tested for electrical stability in this study. However, it is envisaged in this study that the combination of the vacuum swing and the pressure swing desorption method could probably lead to a higher desorption efficiency of the amine-grafted polymer-based adsorbent studied.

2.8 Challenges Facing CCS

2.8.1. Economic Challenges

The implementation of CCS technology has been hindered mainly by financial constraints. The prices of incorporating CCS in power systems ranges between 30% and 70% depending on the method of CO_2 capture used (Karayiannis et al., 2014; Rao and Kumar, 2014). Bowen (2010) and Davies et al., (2013) opined that the challenges facing the implementation of CCS globally centres on economic, social and legal barriers; economic barriers in the sense that CCS is expensive and cannot be implemented by most developing countries. Nonetheless, fast developing nations that have good economic frameworks and policies for successful implementation of CCS in its coal-fired power plants can surmount this challenge. There has also been some scepticism with regards to the deployment of CCS technology in most developing countries; it has been debated that the implementation of CCS will threaten most country's efforts of developing renewable and sustainable energy resources because they also require huge financial incentives (Fu and Gundersen, 2012; Vaccarelli et al., 2014). Nevertheless, the CO_2 generated from most coal-fired power plants is causing many challenges associated with environmental pollution and health hazards. It is imperative to establish regulatory frameworks that will oversee this technology in most developed countries of the world (Bielicki et al., 2014). Moreover, some of the economic barriers could be overcome by creating CCS financing mechanisms, whereby CO_2-emitting industries could contribute towards its financial

development. A collaborative effort between various stakeholders can also accelerate its implementation (Smit et al., 2014).

2.8.2. Environmental Challenges of CCS

There are many environmental concerns associated with CCS; these include contamination of groundwater as a result of CO_2 leakage and the occurrence of earthquakes that might be caused by the sequestrated CO_2 due to pressure build-up (Štefanica et al., 2016). The sequestrated CO_2 might be leaked into the atmosphere if it is stored in underground rocks and therefore escalates the problems of climate change. In addition, leakage could negatively affect soil quality; trees and other vegetation if stored underground (Strube et al., 2011). In most developing countries, this challenge could be surmounted because apart from storing the captured CO_2 in underground rocks, it can also be stored in the available basins. There are abundant geological formations and un-mineable coal fields globally where captured CO_2 can be stored without infringing on environmental safety (Koornneef et al., 2011).

2.8.3. Social Challenges facing CCS

The implementation of CCS may invigorate public debate because this technology is relatively new and thus requires extensive research. Its long-term effect on the environment and people is not yet fully known. However, public awareness is essential in order to highlight its advantages, such as mitigation of CO_2 emissions and environmental degradation. This might in turn stimulate the interests of various stakeholders, which might contribute towards its implementation (Modiko et al., 2014).

2.9 Mathematical Modelling and CO_2 Capture

Mathematical modelling is the application of mathematical and/or statistical methods to analyse complex real-world problems in order to make predictions about what might happen with various actions (Austgen et al., 1989). Solutions to a mathematical model in most studies depend on initial conditions and model assumptions. The steps involved in modelling a process (e.g. for CO2 capture) are depicted in Figure 2.7;

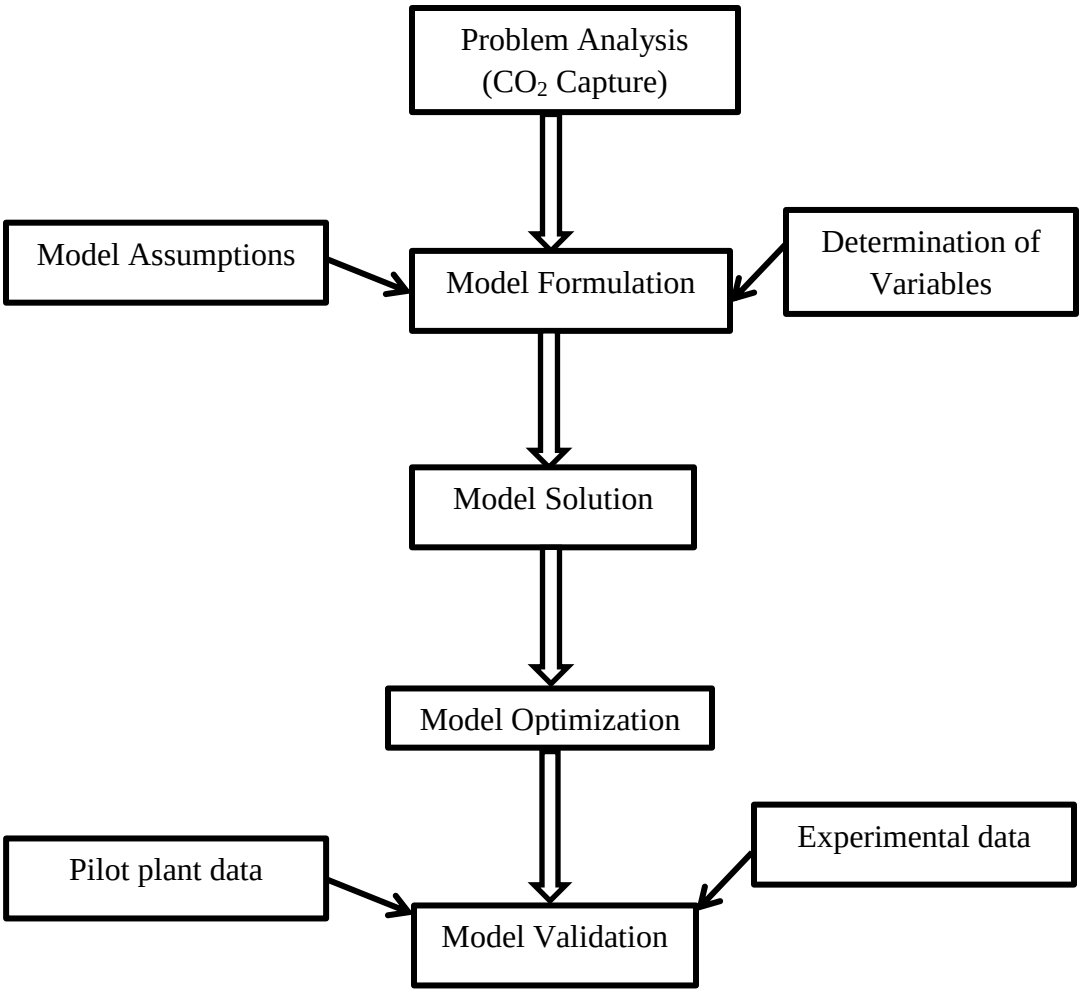


Figure 2.7 Steps involved in modelling a CO_2 capture process

Development of mathematical models which form a better representation of real processes is the basis for the further development of simulation software (Gani and Pistikopoulos, 2002). Model development is done in chemical engineering and also in control engineering for the improvement of mathematical simulation techniques. Process simulation is a model-based representation of chemical, physical, biological, and other technical processes and unit operations in software. The Basic prerequisites for development of process models are a thorough knowledge of the chemical and physical properties of pure components and mixtures involved in the reactions, and mathematical models which in combination allows for the calculation of a process using computers (Rhodes, 1996). Process simulation is used for the scale-up, design, development, analysis, and optimization of technical processes such as: chemical plants, environmental systems, power stations, complex manufacturing operations, biological processes, and similar technical functions (Khan et al., 2011).

Models are used in separation process simulation to introduce assumptions and approximations and also to allow for the description of system properties over a wide range of temperature and pressure which might not easily be solved using real data. The use of predictive methods in process modelling and simulation is much cheaper than experimental work; predicted properties are normally only used in the early steps of the process development to find first appropriate solutions and to exclude wrong pathways (Mallya et al., 1997). Process simulation has encouraged further development of mathematical models in the fields of numeric and the solving of complex problems (Saeger and Bishnoi, 1986).

This study is not focused on model development, but seeks to employ existing adsorption models to describe the behaviour of polyaspartamide during post- combustion CO_2 capture. The outcome of this study is expected to provide useful information, such as kinetic data, that could be used to design an adsorption process based on the polyaspartamide adsorbent. It will also provide information on the understanding of the behaviour of polyaspartamide, which could be employed to scale-up or optimize the adsorbent for industrial applications during CO_2 capture.

2.9.1 Mathematical modelling and Numerical Simulation in CCS

A general approach for modelling gas adsorption and absorption with chemical reaction was proposed by Nikolaidis et al (2016). In the model, simultaneous mass and energy transfer across the interface and the adsorption column were modelled by means of a rate equation and mass transfer coefficients. Previous studies have shown that mathematical models are capable of giving a better prediction of the kinetics, temperature and concentration profiles of the adsorbent which indicates the adsorbent's behaviour during the adsorption process (Afzal et al., 2010; Lim et al., 2013). Gilassi and Rahmanian (2015) carried out mathematical modelling and numerical simulation of CO_2/CH_4 separation in a polymeric membrane (Polytetrafluoroethylene). The authors concluded that the change in CO_2 concentration of the feed greatly affects the permeate concentration both by the diffusion and convection transfers. However, this study seeks to carry out mathematical modelling and numerical simulation of the CO_2 adsorption behaviour of polyaspartamide as an adsorbent during CO_2 capture. The behaviour of the adsorbent will be assessed numerically by considering its kinetic behaviour, pore diffusion, adsorption mechanism, its behaviour in the presence of moisture and effects of other operating parameters on the adsorbent.

A numerical simulation is a mathematical solution run on a computer via a program or codes that implements a mathematical model for a physical system. Numerical simulations are required to investigate the behaviour of materials, processes or systems whose mathematical models are too complex to provide analytical solutions, as in most nonlinear systems (Chavez et al., 2009). In modelling the performance and adsorption behaviour of polyaspartamide during post combustion CO_2 capture in this research, gas-solid kinetic, film diffusion and rate-limiting step models were extensively explored. In this study, the mathematical solution was run in MATLAB R2014a, codes were written in MATLAB to run these simulations and they are presented in the appendix section of this dissertation.

2.9.2 Gas-Solid Adsorption Models

Several gas-solid adsorption models have been reported in literature (Chu, 2010; Dantas et al., 2011; Nikolaidis et al., 2016). The models can be used to study the behaviour of adsorbents during any gas-solid adsorption process. The Elovich model, Avrami model and the Lagergren's pseudo 1^{st} and 2^{nd} order models are popular kinetic models being used to study the kinetic behaviour of solid sorbents (Zhiwu et al., 2013). However, the Elovich model is mainly used to describe chemisorption properties of adsorbents. The gas solid adsorption models developed by Bohart and Adams (Bohart and Adams, 1920), Zhang and Cheng, Clark and Thomas can be used to describe the breakthrough behaviours during most gas-solid adsorption processes. Another model widely used is the Boyd's film diffusion model developed by Boyd et al (1947) which is commonly used to investigate film diffusion properties of solid sorbents as well as the inter and intra molecular diffusion models which is mostly used to determine the actual rate-limiting step controlling the adsorption of gases onto solid sorbents. This study explored the Bohart-Adams model and the Thomas model to understand the breakthrough behaviour of polyaspartamide during CO_2 capture. The Lagergren's pseudo 1^{st} and 2^{nd} order models as well as the Avrami kinetic models were used to report the kinetics of adsorption of CO_2 onto polyaspartamide in this study while the Boyd's diffusion model as well as the inter and intra particle diffusion models were used to investigate the adsorption mechanism of CO_2 onto polyaspartamide as well as the rate-limiting steps controlling the adsorption of CO_2 onto polyaspartamide.

2.9.3 Breakthrough Curve

Breakthrough curve is a plot of relative concentration of an adsorbate against time during adsorption. That is, a plot of the concentration of an adsorbate at a given time (C_t) divided by the initial concentration (C_o) i.e. C_t/C_o versus time. The time for the breakthrough appearance and the shape of the curve are important characteristics in determining the operation and the response of an adsorption column (Han et al., 2009). The Bohart-Adams model and Thomas model have been widely and successfully reported in literature for breakthrough curve modelling (Gholami et al., 2010; Ghribi and Chlendi, 2011). Hence they were considered in this study.

2.9.4 Bohart-Adams Model

The Bohart-Adams model is based on the surface reaction theory and the model assumes that equilibrium is not instantaneous and the rate of adsorption is proportional to the adsorption capacity of the adsorbent (Bohart and Adams, 1920). The Bohart-Adams model was fit to assess breakthrough behaviour in this study because its underlying assumption fit into the required assumptions considered in this study. It establishes the fundamental equation describing the relationship between C/C_o and time (t) in a continuous system. The model was then used to describe the breakthrough curve in which the model parameters such as the maximum adsorption capacity q_s and the adsorption coefficient K were obtained.

The mass balance equation for the Bohart-Adams model is given as:

$$\frac{\partial c}{\partial t} + \frac{v\partial c}{\partial z} + \frac{(1-\varepsilon)\partial q}{\partial t} = 0 \qquad (2.1)$$

The kinetics of adsorption is described by a quasi-chemical rate law which is similar to a pseudo 1st order kinetic model as shown in equation 2.2:

$$\frac{\partial q}{\partial t} = KC\,(q_e - q) \qquad (2.2)$$

Where C is the adsorbate concentration in the gas stream (g adsorbate/L gas), t is time (s), v is superficial velocity of the gas stream (mm/s), x is distance from the column inlet, ε is bed porosity (dimensionless), q_e is concentration at equilibrium and q is the adsorbate concentration in the adsorbent (g adsorbate/g adsorbent).

The assumptions made for the Bohart-Adam's model are:

1. Rectangle or step isotherm is assumed for the model and adsorption bed is homogenous
2. Gradients occur only in the axial direction and they are negligible
3. At time t=0 , the bed is free of adsorbate (CO_2)
4. The model assumes that equilibrium is not instantaneous
5. Irreversible adsorption isotherm

On assuming a negligible axial dispersion as seen in the assumptions above, the differential mass balance equation was solved by Cooney, (1999) as :

$$\frac{\boldsymbol{C}}{\boldsymbol{Co}} = \frac{\mathrm{eT}}{\mathrm{eT} + \mathrm{e}\boldsymbol{\xi} + \mathbf{1}} \tag{2.3}$$

But, $\mathrm{T} = KC_o\left(t - \frac{z}{v}\right)$ and $\boldsymbol{\xi} = \frac{\boldsymbol{Kq_sZ}}{\boldsymbol{v}}\left(\frac{\mathbf{1}-\varepsilon}{\varepsilon}\right)$ (2.4)

Equation (2.3) can be fit to breakthrough data to obtain the values of K and q_s. T is defined as dimensionless time and ξ is a dimensionless distance.

Reciprocating and mathematically solving Equation (2.3) yields,

$$\frac{\boldsymbol{Co}}{\boldsymbol{C}} = \frac{\boldsymbol{e}^{\mathrm{T}}}{\boldsymbol{e}^{\mathrm{T}}} + \frac{\boldsymbol{e}\,\boldsymbol{\xi}}{\boldsymbol{e}^{\mathrm{T}}} - \frac{\mathbf{1}}{\boldsymbol{e}^{\mathrm{T}}} \tag{2.5}$$

At long times, the term $\frac{\boldsymbol{z}}{\boldsymbol{v}}$ in the expression for T in Equation (2.3) can be neglected.

$$\ln\left(\frac{C_o}{C}\right) = \frac{\mathrm{K}q_s\mathrm{Z}}{\mathrm{v}}\left(\frac{1-\varepsilon}{\varepsilon}\right) - \mathrm{KC_o t} \tag{2.6}$$

Since the bed is assumed to be homogeneous,

$$\ln\left(\frac{C_o}{C}\right) = Kq_s.\frac{Z}{v} - KC_o t \tag{2.7}$$

$$\ln\left(\frac{C}{C_o}\right) = KC_o t - Kq_s.\frac{z}{v} \tag{2.8}$$

Equation (2.8), which is a linearized form of Equation (2.1), is the Bohart-Adams model as derived from mass balance equations. A plot of $\ln\frac{C}{C_o}$ against 't' will produce a linear graph and

the model parameters which is the maximum adsorption capacity q_s and the adsorption coefficient K can be obtained from intercept and slope of the graph, respectively.

2.9.5 Thomas model

Thomas model is one of the oldest and most widely used models to describe gas-solid adsorption processes. Its behaviour is similar to that of the Langmuir isotherm and the adsorption kinetics is governed by a second-order reversible reaction kinetics (Trgo et al., 2011). The maximum adsorption capacity of an adsorbent and the breakthrough curve or concentration-time profile is very important in designing a column for an adsorption process. The Thomas model is used in most designs to predict the concentration-time profile and the maximum adsorption capacity of an adsorbent. Thomas model alongside other gas-solid adsorption model has been used in previous studies to describe the breakthrough curve during the adsorption of organic dye onto natural clay in a fixed bed adsorption column (Ghribi and Chlendi, 2011). The authors however concluded that the initial region of breakthrough was adequately described by the Adams-Bohart model at all experimental conditions studied while the full description of the breakthrough curve was described by Thomas, Yoon-Nelson and Clark models. On this note, Thomas model was adapted in this study to investigate the breakthrough behaviour of a novel adsorbent (polyaspartamide) during the adsorption of CO_2 onto polyaspartamide material. The model described the breakthrough time and equilibrium concentration of CO_2 for the adsorption process in this study.

Basic assumptions made for the Thomas model are:

1. The axial and radial dispersion in the column is negligible
2. Constant separation factor
3. Adsorption is described by a pseudo-second order reaction rate principle and reduces to a Langmuir isotherm at equilibrium.
4. The column void fraction is constant
5. Constant temperature and pressure process conditions
6. Negligible external resistance during mass transfer process.

The Thomas model takes the form of:

$$\frac{C}{Co} = \frac{1}{1 + e^{\left[\frac{K_{th}}{Q(q_o.X - Co\ Veff)}\right]}} \quad (2.8.1)$$

Where K_{th} = Thomas rate constant (ml $min^{-1}mg^{-1}$), q_o = Amount of CO_2 adsorbed, X = mass of the adsorbent (g), V_{eff} = Effective volume and Q = Flowrate (ml/s).

On linearizing the model and taking natural logarithms, equation (2.8.1) yields:

$$\ln\left(\frac{C}{Co} - 1\right) = \frac{K_{th}.q_o.X}{Q} - \frac{K_{th}.C_o}{Q}.\ V_{eff} \quad (2.9)$$

Equation (2.9) is the linearized form of the Thomas model. The model parameters q_o and Kth can be determined from the graph of $\ln\left(\frac{C}{Co} - 1\right)$ versus Veff at a given flow rate Q. The Thomas model is widely used to explain column performance (Thomas, 1994).

2.9.6 Summary

There are various barriers facing the implementation of CCS globally. Nonetheless, it can be concluded that high CO_2 emitting nations are working tirelessly towards curtailing their carbon footprint by shifting focus to major sources of CO_2 emission, such as coal-fired thermal power plants. More so, most countries have included CCS policies into their legislation for possible implementation. This clearly brings to light the huge potential of implementing CCS in coal-fired thermal power plants. The pressing challenges related to CO_2 emissions necessitate the search for clean and sustainable energy technologies. The potential for CO_2 capture lies in the major emitting sources, which are the electricity-generating coal-fired power plants. The most suitable CO_2 capture route for coal-fired power plants is post-combustion CO_2 capture, because it allows for easy retrofitting of capture systems in the existing coal-fired power plants. Adsorption technology using solid polymer-based adsorbents will be ideal and more economically viable for CO_2 capture in coal-fired power plants. Given the fact that the post-combustion CO_2 capture technology is highly embraced, its overall system performance with regards to typical coal-fired power plants can be assessed by using pilot-plant or experimental results from these power plants, and these results should be validated for their accuracy. Since adsorbents are very vital to adsorption technology, it is necessary to understand the behaviour of these adsorbents under

different conditions in order to prepare it for a wider use. Mathematical modelling is a very important and cost-effective tool used during the investigation of the behaviours of adsorbents as it is capable of describing the behaviour of adsorbents in every part of the adsorption column. Outcome of the models if validated with experimental or pilot plant data can be used to scale up, optimize or design an efficient CO_2 adsorption system for industrial applications.

This study is dedicated to investigating the CO_2 adsorption behaviour of polyaspartamide during post-combustion CO_2 capture using experimental study and mathematical modelling approach. Experimentally obtained data will be used to validate the model results. The kinetic data obtained can be used to scale-up, optimize or design a CO_2 adsorption system that uses polyaspartamide as an adsorbent.

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CHAPTER THREE

Experimental and Modelling Procedure

3.1 Introduction

In order to have a better understanding of the CO_2 adsorption behaviour of polyaspartamide as an adsorbent during CO_2 capture, numerical simulations were performed to describe adsorption of CO_2 onto polyaspartamide via mathematical modelling and experimental study approach. Experimentally obtained data were fit into existing gas-solid adsorption models in order to describe the adsorption of CO_2 on polyaspartamide in this study and to investigate the adsorption kinetics, diffusion mechanism, mass transfer limitation and parametric effect of various operating variables on the performance of polyaspartamide as an adsorbent during CO_2 capture. Gas adsorption experiments can be carried out in a thermogravimetric analyser (TGA), packed bed adsorption column, fluidized beds etc. Similarly, during the development of CO_2 capture and storage processes, modelling plays an important role. Selecting an appropriate model for CO_2 capture is also very important, because of the large range of technology options, the difference in technology development stage, and the different purposes for which a process model can be used (Van der Spek and Ramirez, 2014). Models can be used for performance assessment, process optimization, and even processing design. In this study, CO_2 adsorption experiments were carried out in a packed bed adsorption column in order to create a direct contact between the gas and the adsorbent. Every model outcome is a prediction and needs to be validated. Model results can be validated using experimental data, pilot plant data or data obtained from literature. The model results in this study were validated using experimental data. That is, CO_2 adsorption experiments were conducted and the results were used to validate the models.

3.2 Prior study

The synthesis and characterization of polyaspartamide which is the adsorbent considered in this study has been carried out and reported in literature (Chitsiga et al, 2016). Nuclear Magnetic Resonance analysis was carried out on the adsorbent (polyaspartamide) by Chitsiga et al. (2016) to confirm if the synthesis of the adsorbent was qualitatively successful. Among other analyses carried out on this adsorbent were Fourier Transform Infrared Spectroscopy (FTIR) to determine all the functional groups present in the adsorbent, Thermogravimetric analysis (TGA) to

determine the thermal stability of polyaspartamide, Scanning Electron Microscopy (SEM) was carried out to obtain clear images of the synthesized adsorbent and BET analysis was carried out on polyaspartamide to determine its pore size, pore volume and BET surface area (Chitsiga et al., 2016). Analytical results for this adsorbent were adequately reported in literature. As such, these analyses will not be reported in this dissertation to avoid undue repetitions. However, apart from the synthesis and characterization of this material that was reported by Chitsiga et al. (2016), the experimental aspect of this work used to generate the data employed in the validation of the model results was conducted by me. The behaviour of this material (polyaspartamide) during post combustion CO_2 capture was investigated using the experimental study, mathematical modelling and numerical simulation approach to provide new information about the adsorbent as these were not clearly reported by Chitsiga et al. (2016).

3.3 CO_2 Adsorption Experiment and Modelling

3.3.1. CO_2 Adsorption Experiments

Polyaspartamide which is also known as an amine grafted polysuccinimide was used as the adsorbent in this study. Information regarding the synthesis and characterization of this adsorbent was reported elsewhere (Chitsiga et al., 2016). Polyaspartamide was obtained by reacting polysuccinimide (the root polymer) with Ethylenediamine (EDA), N, N-Dimethylformamide (with DMF > 99 %), Acetone and Ethyl Ether purchased from Sigma-Aldrich (Pty) South Africa.

For the preliminary investigation conducted which forms an extended part of this study, a chitosan-impregnated sodalite-zeolite metal organic framework material was used. Sod-ZMOF/Chitosan was synthesized from a modified protocol described in literature (Chen et al., 2011). Detailed information regarding the synthesis and characterization of sod-ZMOF/Chitosan considered in this study was reported in a different study. As such, it will not be reported again in this study. Sod-ZMOF was synthesized using the method adapted from the work reported in literature (Chen et al., 2011).

A balanced mixture of 15% CO_2 and 85% N_2 was used to mimic a flue gas source in this study. 100% N_2 was then used to degas the adsorption column during the experiment to get rid of

impurities. All gases used in this study were purchased from Afrox (pty) South Africa. CO_2 concentrations were taken directly from the CO_2 gas analyser.

Continuous gas-solid adsorption experiments were conducted in a laboratory-scale packed bed adsorption column to validate the model results. 0.1 g of polyaspartamide was fed into the packed bed adsorption column and the temperature of the adsorption bed was raised to 373 K in order to get rid of moisture from the adsorbent if present. Pure Nitrogen was then passed through the bed to degas the adsorption system and get rid of impurities on the adsorbent. After degassing the adsorption system with nitrogen, the temperature was lowered to 333, 318 and 303 K, respectively. A gas mixture containing 15% CO_2 and 85 % N_2 was fed into the adsorption column while by-passing the reactor in order to measure the initial concentration of CO_2 in the gas mixture. The initial concentration of CO_2 in the gas mixture was determined from the CO_2 gas analyser. The gas mixture was then allowed to flow through the reactor at isothermal conditions. The concentration of CO_2 in the adsorption column was recorded from the CO_2 gas analyser as it changes with time until equilibrium was attained. The experiment was allowed to run for 1200 seconds (20 minutes) at every temperature. The feed gas flow rate was 2.5 ml/s. After every run, the reactor was opened and the adsorbent was changed. A fresh polyaspartamide material (0.1 g) was fed into the packing to continue the adsorption experiment. The operating pressure was also varied from 0.5 – 2 bar at constant temperature and flow rate to study the effect of pressure on the adsorption capacity of polyaspartamide. Effect of gas flow rate on the adsorption behaviour of polyaspartamide was also investigated when the flow rate was varied (2.5, 2.0 and 1.5 ml/s). The experimental process is depicted by a process flow diagram in Figures 3.1.

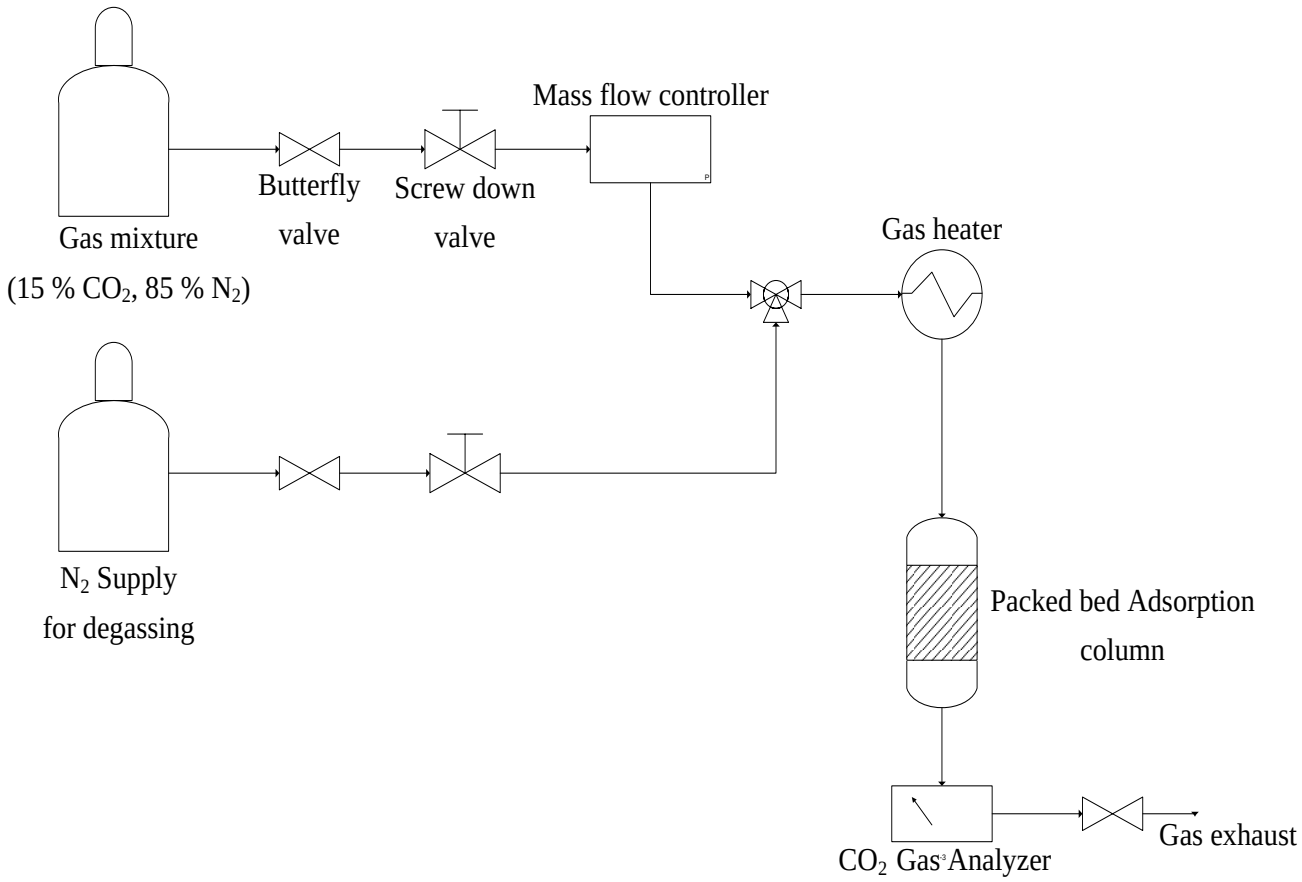


Figure 3.1 Experimental flow diagram for CO_2 adsorption on polyaspartamide.

3.3.2 Modelling

A modelling and experimental study approach was considered in this study. Existing kinetic, non-kinetic and rate limiting step models were explored to study the behaviour of these adsorbents. Experimental data were fit to these existing models. Gas-solid adsorption models were explored in this study to describe the adsorption behaviour of CO_2 onto polyaspartamide. Models were solved numerically; programming codes were written in MATLAB R2014a for both experiments and models considered. The model output was then compared with the experiment in MATLAB. The model that appeared to be in close agreement with the experiment was considered as the model best describes the behaviour of the adsorbent. Kinetic and diffusion models were explored in this dissertation.

3.3.2.1 Kinetic Modelling

Lagergren's pseudo 1st order, pseudo 2nd order and Avrami kinetic models were used to model the kinetics of adsorption of CO_2 onto polyaspartamide in this study by fitting experimental data into the linearized form of these kinetic models. Simulation was done in the MATLAB R2014a environment. Kinetic parameters which are very important for design and optimization purposes were obtained from the solutions in MATLAB. The kinetic study was carried out to investigate the behaviour of polyaspartamide with time under various adsorption conditions.

Existing gas-solid adsorption models proposed by Bohart-Adams and Thomas were used to model the breakthrough behaviour of polyaspartamide during post-combustion CO_2 capture. Experimentally obtained data were also fit into the models and the model results were validated.

3.3.2.2 Diffusion Mechanism

The mechanism of diffusion of CO_2 onto polyaspartamide during CO_2 capture was investigated using the Boyd film diffusion model. Film and pore diffusion was also investigated using this model. Inter and intra molecular diffusion models were used to describe the rate-limiting step controlling the adsorption of CO_2 onto polyaspartamide in this study. Data obtained from experiments conducted were fit into the diffusion models and validated.

3.3.2.3 Rate-limiting Step

Previous studies have used several models to determine the actual rate-limiting step controlling the adsorption of gases onto solid sorbents. (Song et al., 2016). In this study, the inter-particle and intra-particle diffusion models as derived from the Boyd's diffusion model were adapted from previous studies (Viegas et al., 2014; Song et al., 2016) and used to investigate the actual rate limiting step controlling the adsorption of CO_2 onto polyaspartamide

3.3.2.4 Parametric Effect

Parametric effects of temperature, operating pressure and gas flow rates on the behaviour of polyaspartamide were investigated in this study experimentally by varying those parameters with time and measure the amount of CO_2 that was adsorbed by PAA with a change in parameter values. Temperature was varied in the range of 303-333 K; pressure was varied from 0.5-2.5 bar

while flowrate was varied between 1-2.5 ml/s. Same experimental conditions were imputed into the models and solved. The effect of moisture was investigated numerically using a modified Mane's model derived from the Polanyi equation. Results were simulated in the MATLAB R2014a and necessary conclusions were made.

3.3.3 Model Description

The mathematical models explored in this study were existing gas-solid adsorption models derived from the mass balance around the adsorption column. Their basic assumptions are presented in Table 3.1. Complete set of mathematical models capable of describing the CO_2 adsorption behaviour of polyaspartamide for post combustion CO_2 capture based on ordinary differential and algebraic equations which were studied based on the underlying physical principles governing the behaviour of the gas-solid adsorption process. Kinetic data of the adsorption process is another characteristic that is very important for the simulation and design of a CO_2 capture system. This is because, kinetic data significantly influence the residence time required for the completion of any adsorption process as well as the unit capital cost (Serna - Guerrero and Sayari, 2010). In this study, the kinetics of adsorption of Sod-ZMOFs/Chitosan was investigated using the Lagergren's pseudo 1^{st} and 2^{nd} order kinetic models. Variety of gas-solid adsorption models with different level of complexities to quantitatively describe the behaviour of several adsorbents during CO_2 adsorption process have been studied and reported in literature (Cheung et al, 2001). Due to complexities associated with the description of model parameters, this study considered a common approach which involves curve fitting of the data obtained from experiments to a number of kinetic models. The model that correlates well with the experimental data is always considered as the best model describing the behaviour of the adsorbent.

The CO_2 adsorption breakthrough curves in this study were obtained by plotting the ratio of the concentration of CO_2 exit at time to the initial concentration of CO_2. The breakthrough curves were obtained at various temperatures, constant pressure and constant flow rates. The breakthrough curves in this study were described using the Bohart-Adams model (Bohart and Adams, 1920). The model results obtained from these mathematical models were compared with experimental results in order to validate the models and conclude on which of the models best describe the adsorption behaviour of polyaspartamide during post combustion CO_2 capture.

Model parameters obtained from the solution in MATLAB R2014a described the adsorption capacity of the adsorbent and it was validated with experimental data.

Previous studies have presented several kinetic models to describe the adsorption behaviour of adsorbents (Cestari et al.,2006; Gupta and Bhattacharyya, 2011). Amongst the reported kinetic models, the Lagergren's pseudo 1^{st} order, pseudo 2^{nd} order and Avrami kinetic models are the most widely used because of their simplicity in describing the kinetics of adsorption as well as the interactions between the adsorbent and the adsorbate. The general methodology and various steps considered in this study are depicted in Figure 3.2;

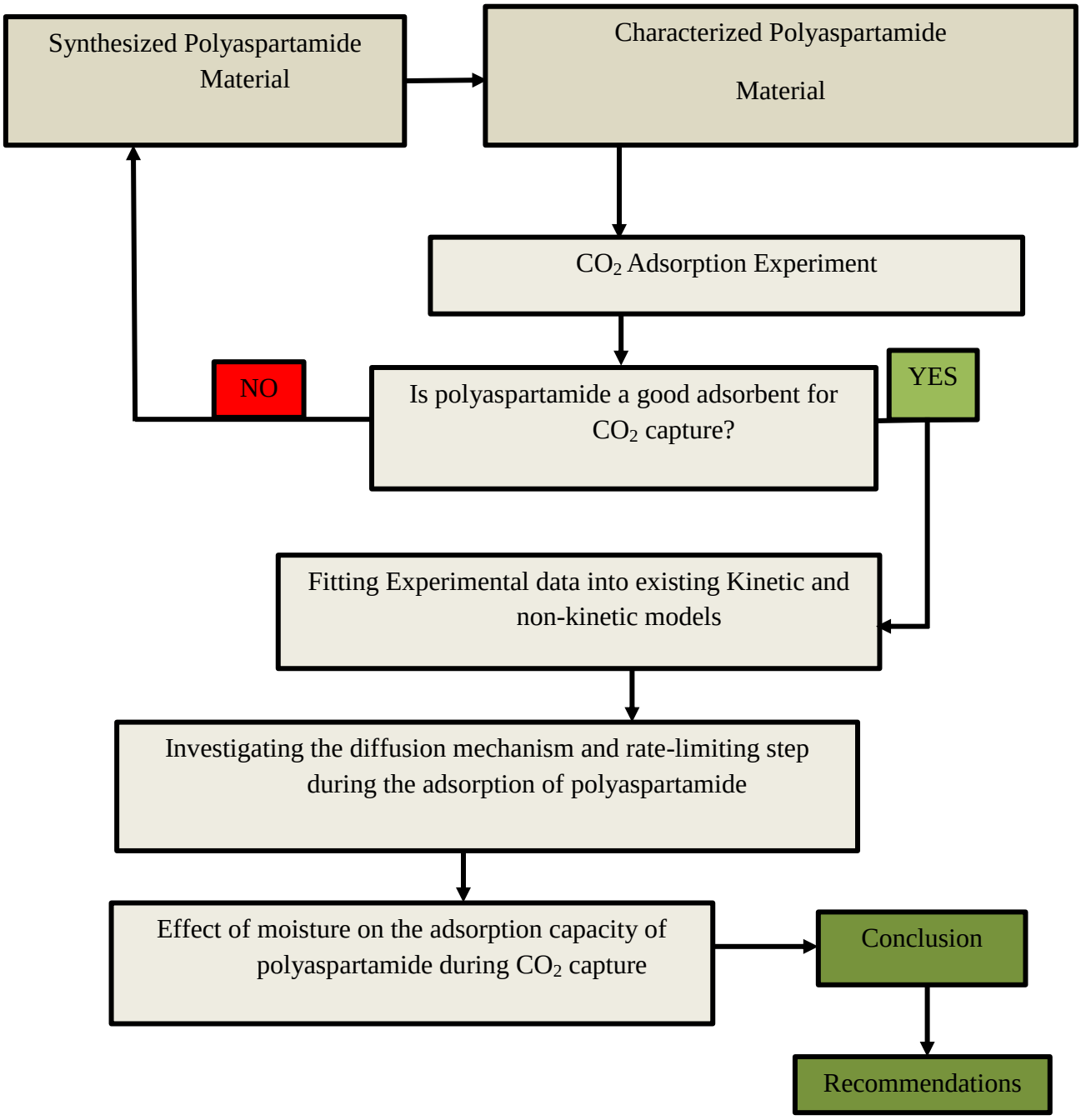


Figure 3.2. General methodology and steps for the study.

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CHAPTER FOUR

Mathematical Modelling of the CO_2 Adsorption Performance of Polyaspartamide: Kinetics and Breakthrough Curves

4.1 Introduction

Thermodynamic and kinetic study play a role in understanding the performance of any adsorbent (Qui et al., 2009). The solute uptake rate which determines the residence time required for completion of the adsorption process can also be established from the kinetic analysis. Several mathematical models have been developed to describe adsorption behaviour of adsorbents during post-combustion CO_2 capture. Due to the complex nature of the mathematical model solutions, the use of accurate and simplified models have been explored to reduce the computational time (Sun et al., 2015). Mathematical modelling of adsorption processes have attracted a considerably high attention amongst researchers today because mathematical models are capable of estimating the breakthrough curve, adsorption kinetics and temperature profile for a certain adsorbent and adsorbate in all locations within the adsorption column (Shafeeyan et al., 2014; Sun et al., 2015; Plaza et al., 2016). The model, if experimentally verified can be used to study the effect of various process parameters such as pressure, temperature, flow rate and concentration on the adsorption behaviour of an adsorbent. CO_2 capture using solid adsorbents involves a selective separation of CO_2 based on a gas–solid interaction (Dantas et al., 2011a). The adsorbent in most adsorption processes is always in contact with the gas in a packed bed adsorption column (Yoo et al., 2015). An understanding of the behaviour and performance of the adsorbent and also the dynamic behaviour of the adsorption system is required for a rational process design, scale-up and optimization (Xu et al., 2013; Chowdhury et al., 2012).

In recent times, several adsorbents have been synthesized and investigated for CO_2 capture using experimental and modelling approach (Aziz et al., 2014; Dantas et al., 2011; Sekoai and Yoro.,2016). Examples are synthetic zeolites, activated carbon, carbon molecular sieves, silica, metal oxides, chitosan, carbon nanotubes, sodalite zeolite metal organic frameworks (Sod-ZMOFs) etc. Before designing an adsorption process, selecting an appropriate adsorbent with high working capacity as well as a strong desorption capability is key for post combustion CO_2 capture (Xu et al., 2013). This simply means that adsorbents play a key role in any adsorption

technology (Gibson et al., 2016). For instance, adsorbents determine the overall CO_2 capture performance in the vacuum swing adsorption (VSA) technology (Chaffee et al., 2007). The key elements for a good adsorbent in CO_2 capture technology are; high selectivity of CO_2 , high adsorption capacity, rapid adsorption/desorption kinetics, stable adsorption capacity after repeated cycles and adequate mechanical strength of the particles (Gale et al., 2009; Yoro and Sekoai.,2016). Amine-modified polymer-based adsorbents have been developed recently (Creamer et al., 2016). Polyaspartamide has been studied as a potential adsorbent for post-combustion CO_2 capture (Ngoy et al., 2014). Polyaspartamide (PAA) is an amine grafted polymer from polysuccinimide obtained when polysuccinimide reacts with Ethylene diamine (EDA). Polyaspartamide is considered as a potentially good adsorbent for post combustion CO_2 capture because of its large surface area, non-toxic nature, biodegradable nature and its good geometry (Ngoy et al., 2014 ; Chitsiga et al., 2016). The behaviour and performance of polyaspartamide as an adsorbent can be assessed in terms of various desired attributes, such as its equilibrium adsorption capacity, regeneration, multi cycle durability, and adsorption/desorption kinetics. In this study, existing gas-solid kinetic and non-kinetic adsorption models will be used to assess the behaviour of polyaspartamide during post combustion CO_2 capture using a balanced flue gas stream of 15% CO_2 and 85% N_2. This chapter focuses on investigating the adsorption behaviour of polyaspartamide during post- combustion CO_2 capture using mathematical modelling and experimental study. Other properties to test for the performance of polyaspartamide during CO_2 capture such as adsorption breakthrough behaviour and kinetics are also presented in this chapter.

4.2 Experimental and Modelling

4.2.1 Experimental

The adsorbent considered in this study is polyaspartamide. Detailed information about the synthesis and characterization of the adsorbent can be obtained elsewhere (Ngoy et al., 2014; Chitsiga et al., 2016). As such, it will not be repeated in this study. The gas used was a balanced mixture of CO_2 and N_2 (15% CO_2, 85 % N_2) purchased from Afrox (pty) South Africa. The experiment was carried out in a laboratory-scale packed bed adsorption column. Detailed description of the experimental section is provided in Chapter 3 of this dissertation. The experimental conditions and model assumptions for this study are summarized in Table 4.1.

Table 4.1. Experimental conditions for adsorption

Operating conditions	
Adsorption temperatures (K)	303 - 333
Adsorption total pressure (bar)	2
Inlet flow rates (ml/s)	1.5 – 2.0
Inlet gas concentration (vol. %)	15.0
Mass of adsorbent (g)	0.1

4.2.2 Experimental Procedure

Details about the experimental procedure were discussed in chapter three of this dissertation and summarized here as follows; 0.1 g of polyaspartamide was fed into the packing in the adsorption column and degassed by passing in dry Nitrogen gas through the packed bed at an inlet flow rate of 1.5 ml/s and a temperature of 373 K for 1 hour to remove CO_2 that could be present within the adsorption column. Polyaspartamide was heated to 373 K within the adsorption column to remove moisture, other impurities and also improve its porosity. After the degassing and heating stage, the temperature of the adsorption bed was lowered to 303 K under N_2 flow. The flue gas mixture (15% CO_2, 85 % N_2) was fed to the packed bed adsorption column at a flow rate of 2.5 ml/s while by-passing the reactor in order to determine the inlet concentration of CO_2 from the gas analyser (model: ABB-AO2020). The flue gas was then allowed to pass through the reactor containing the adsorbent. The gas flow rate was regulated using a mass flow controller while the CO_2 uptake onto the polyaspartamide material was monitored as a function of time from the CO_2 gas analyser. The experiment was repeated at temperatures of 318 and 333 K and flow rates of 1.5 and 2.0 ml/s to determine the behaviour of the adsorbent at higher temperatures and different flow rates. The experiment lasted for 1200 seconds until equilibrium was attained.

4.3.1 Model description

Table 4 2. Models explored and the basic assumptions made

Models Studied	Assumptions
Bohart-Adams model	1. Rectangle or step isotherm is assumed for the model and adsorption bed is homogenous
	2. Gradients occur only in the axial direction and they are negligible
	3. At time t = 0, the bed is free of adsorbate (CO_2)
	4. The model assumes that equilibrium is not instantaneous
	5. Irreversible adsorption isotherm
Thomas Model	1. The axial and radial dispersion in the column is negligible
	2. Constant separation factor
	1. Adsorption is described by a pseudo-second order reaction rate principle and reduces to a Langmuir isotherm at equilibrium. 4. The column void fraction is constant
	5. Constant temperature and pressure process conditions
	6. Negligible external resistance during mass transfer process.
Lagergren's pseudo 1st order model	1. The rate of adsorption increases as the number of vacant site on the adsorbent increases
	2. Local equilibrium is achieved instantaneously and the primary resistance is mass transfer resistance.
Lagergren's pseudo 2nd order model	1. The rate of adsorption is proportional to the square of the number of vacant sites

The models considered in this study were existing gas-solid adsorption models derived from the mass balance around an adsorption column. Assumptions made for the models are listed in Table 4.2.

4.3.2 Model implementation

Experimental data were fit into the Bohart-Adams model, Thomas model, Lagergren's Pseudo 1st and 2nd order models as well as the Avrami kinetic model, to describe the behaviour of the adsorbent. Kinetic data significantly influence the residence time required for the completion of any adsorption process as well as the unit capital cost (Belmabkhout and Sayari, 2009). The kinetic models used to describe the adsorption kinetics were validated using kinetic data obtained from the experiment conducted. Due to complexities associated with the description of model parameters, this study considered a common approach which involved fitting of the data obtained from experiments to a number of mathematical models. The model that fits best with the experimental data is always considered as the best model describing the behaviour of the adsorbent (Serna-Guerrero and Sayari, 2010). Breakthrough curves in this study were obtained by plotting the normalized concentration of CO_2 (C/C_o) against time. The breakthrough curves were obtained at various temperatures and also different flow rates. The breakthrough curves in this study were described using the Bohart-Adams and the Thomas model (Bohart and Adams, 1920; Thomas, 1944). The model results were validated using the experimental data.

4.4 Results and Discussion

4.4.1 Adsorption behaviour

In order to understand the adsorption behaviour of CO_2 onto polyaspartamide, the adsorbent was experimentally studied under different adsorption conditions such as temperature, pressure and flow rates. The experimental breakthrough curve obtained for the adsorbent is shown in Figure 4.1. The breakthrough curve in Figure 4.1 was obtained at various isothermal conditions (i.e. 303, 318 and 333 K). The shape of the curves exhibited a common behaviour at different adsorption temperature, constant pressure and flowrates. The general shape of the breakthrough curves for the adsorption of CO_2 onto polyaspartamide was achieved as expected; it was similar to breakthrough curves obtained for other polymer-based adsorbents reported in literature (Rezaei et al., 2014; Fan et al., 2014). The breakthrough curve explains that the amount of CO_2 captured by the adsorption sites on polyaspartamide increases with a decrease in adsorption temperature and increased operating pressure. The breakthrough curves depicted in this study showed a plot of the ratio of the final

concentration at the outlet C and the inlet concentration Co against the contact time within the packed bed at different operating pressures and temperatures. The experimental conditions considered in this study are summarized in Table 4.1. The CO_2 adsorption breakthrough time for polyaspartamide occurred at 700 seconds at a pressure of 200 kPa (2bar) and temperature of 303 K. Longer breakthrough times were observed when the temperature was increased to 318 and 333 K. This simply means that the pore diameter of polyaspartamide is sufficient for CO_2 entrapment depending on the operating temperature. The saturation time for adsorption of CO_2 on polyaspartamide was quite long as deduced from the experimental breakthrough curve in Figure 5.1. This could be attributed to the large pore volume of polyaspartamide. The effect of feed flow rate on the adsorption of CO_2 onto polyaspartamide was investigated by operating the adsorption process at different flow rates (1.5 and 2.0 ml/s) at a constant adsorption temperature of 303 K and pressure of 2 bars as shown in Figure 4.2. According to the breakthrough curve in Figure 4.2, at higher flowrates, the packed bed adsorption column was saturated early and lower flow rates resulted in a shallower adsorption zone and longer contact time between the CO_2 and the adsorbent in the packed bed. Early breakthrough time resulted in a less CO_2 uptake by polyaspartamide. The high CO_2 adsorption capacity displayed by polyaspartamide in this study is attributed to the large surface area of the amine grafted polyaspartamide. The Bohart-Adams and Thomas non kinetic models were used to fit the experimental breakthrough curve at 303 K. It was observed that the Bohart-Adams model gave a better fitting with the experimental data as shown in Figure 4.3. This means that external mass transfer dominated the overall system kinetics during the CO_2 adsorption process in this study. In order to determine the accuracy of each model explored in this study, an error function based on the normalized standard deviation adapted from a related study (Borah et al., 2011) was applied as shown in Equation (4.1):

$$\%\text{Err} = \sqrt{\frac{\sum_{i=1}^{N=3}\left(\frac{Q_{exp} - Q_{mod}}{Q_{exp}}\right)^2}{N-1}} \times 100 \qquad (4.1)$$

Where % Err is the error function from the study in percentages, Q_{exp} is the average amount of CO_2 adsorbed experimentally at a given time, Q_{mod} is the amount of CO_2 adsorbed as predicted by the mathematical model and N is the total number of experimental runs.

The CO_2 capture efficiency of the adsorbent was calculated on percentage basis by dividing the equilibrium concentration of CO_2 by the initial CO_2 concentration according to Equation (4.2).

$$\%\ \ CO_2 \text{ capture efficiency} = \frac{C_e}{C_o} \times 100 \qquad (4.2)$$

Where C_e is the gas concentration at equilibrium and C_o is the initial concentration of the gas. The percentage CO_2 capture efficiency was obtained at all temperatures considered in this study using Equation 4.2 and presented in Table 4.3.

Table 4.3 CO_2 capture efficiency of polyaspartamide at different adsorption temperatures and constant pressure.

Temperature (K)	Pressure (bar)	CO_2 capture efficiency (%)
303	2	92.67
318	2	90.00
333	2	86.67

4.4.2 Kinetics of Adsorption

Apart from the fact that a good adsorbent is expected to have fast adsorption kinetics, kinetic data of the adsorption process is another characteristic that is very important in the design of a CO_2 capture system. The Lagergren's pseudo 1st order, pseudo 2nd order and Avrami kinetic models were used to investigate the kinetics of adsorption CO_2 onto polyaspartamide as presented in Figure 4.4. The Lagergren's pseudo 1st and 2nd order kinetic models had some limitations with respect to the adsorption of CO_2 onto polyaspartamide. After few seconds, the Lagergren's pseudo 1st order model under-estimated the uptake of CO_2 till about 120 seconds and afterwards, CO_2 uptake was still under-estimated consistently until the adsorption process attained equilibrium. The pseudo second order model also did not

perfectly fit into the experimental data. This therefore suggests that the Lagergren's pseudo 1st order model which described mainly the early stage of adsorption is applicable only under low surface coverage as previously reported in literature (Ho and McKay, 1998; Chueng et al., 2001; Guo, et al., 2006; Ho, 2006; Gupta and Bhattacharyya, 2011; Song, et al., 2016). However, the best fit for the adsorption kinetics was consistently obtained at different temperatures with the Avrami kinetic model because of the model's ability to account for CO_2 adsorption by both physical and chemical adsorption as shown in Figure 4.4. Going by the results of the Avrami kinetic model in this study, the adsorption of CO_2 onto polyaspartamide could be described as a physiochemical process. The kinetic constant of the Avrami model is independent of the initial concentration of CO_2. The kinetic models and their corresponding parameters are presented in Table 4.4. The Avrami kinetic model consistently displayed the least percentage error at all temperatures studied as seen in Table 4.3. Hence, it could be inferred that the kinetics of adsorption of CO_2 onto polyaspartamide was best described by the Avrami kinetic model. The kinetic parameters presented in Table 4.3 can be useful in designing and optimizing a CO_2 adsorption system using polyaspartamide as an adsorbent.

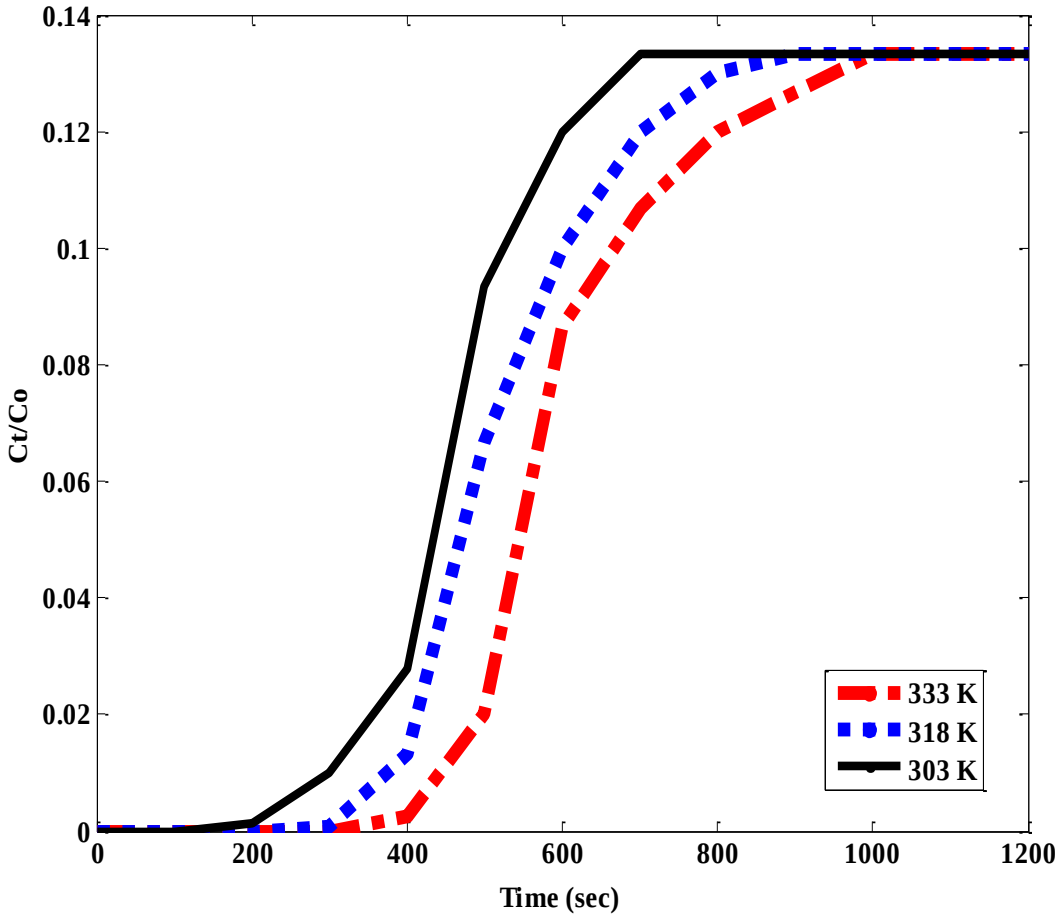


Figure 4.1 Experimental breakthrough curves (Conditions: Pressure 2 bar, Temperature: 303-333 K)

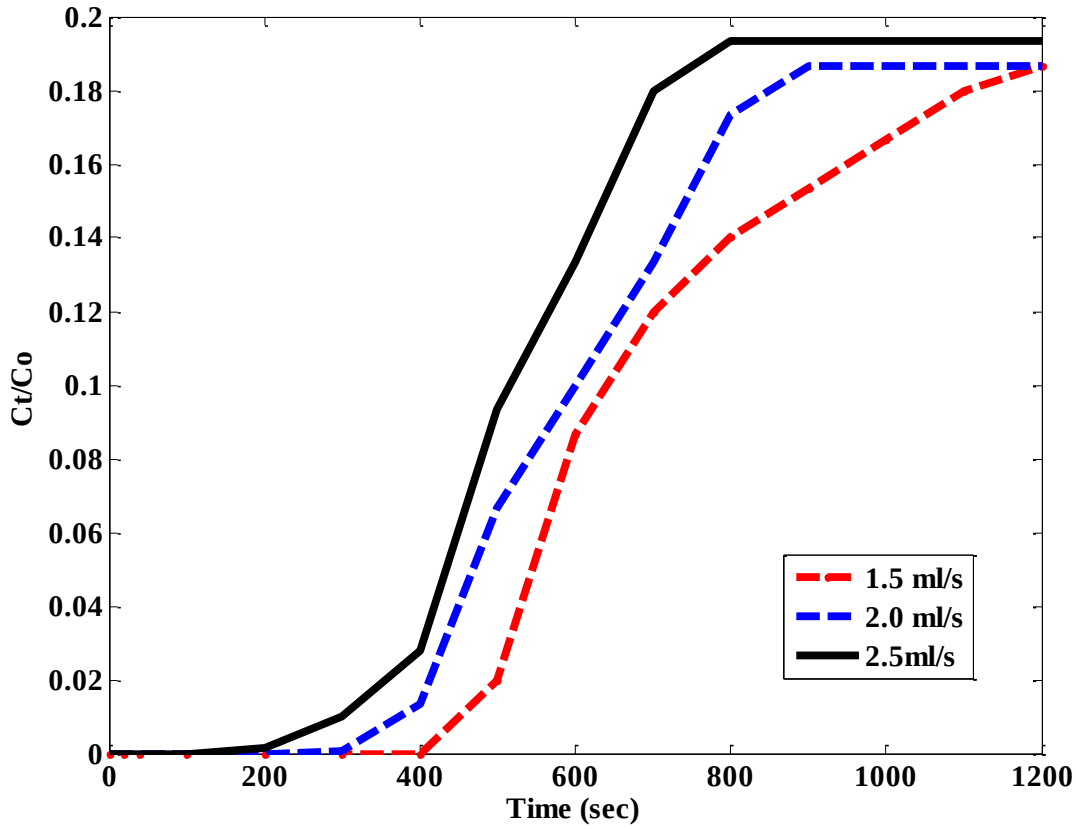


Figure 4.2 Effect of feed flow rate as a function of time. (Experimental conditions: feed pressure, 2 bar, and temperature 303 K).

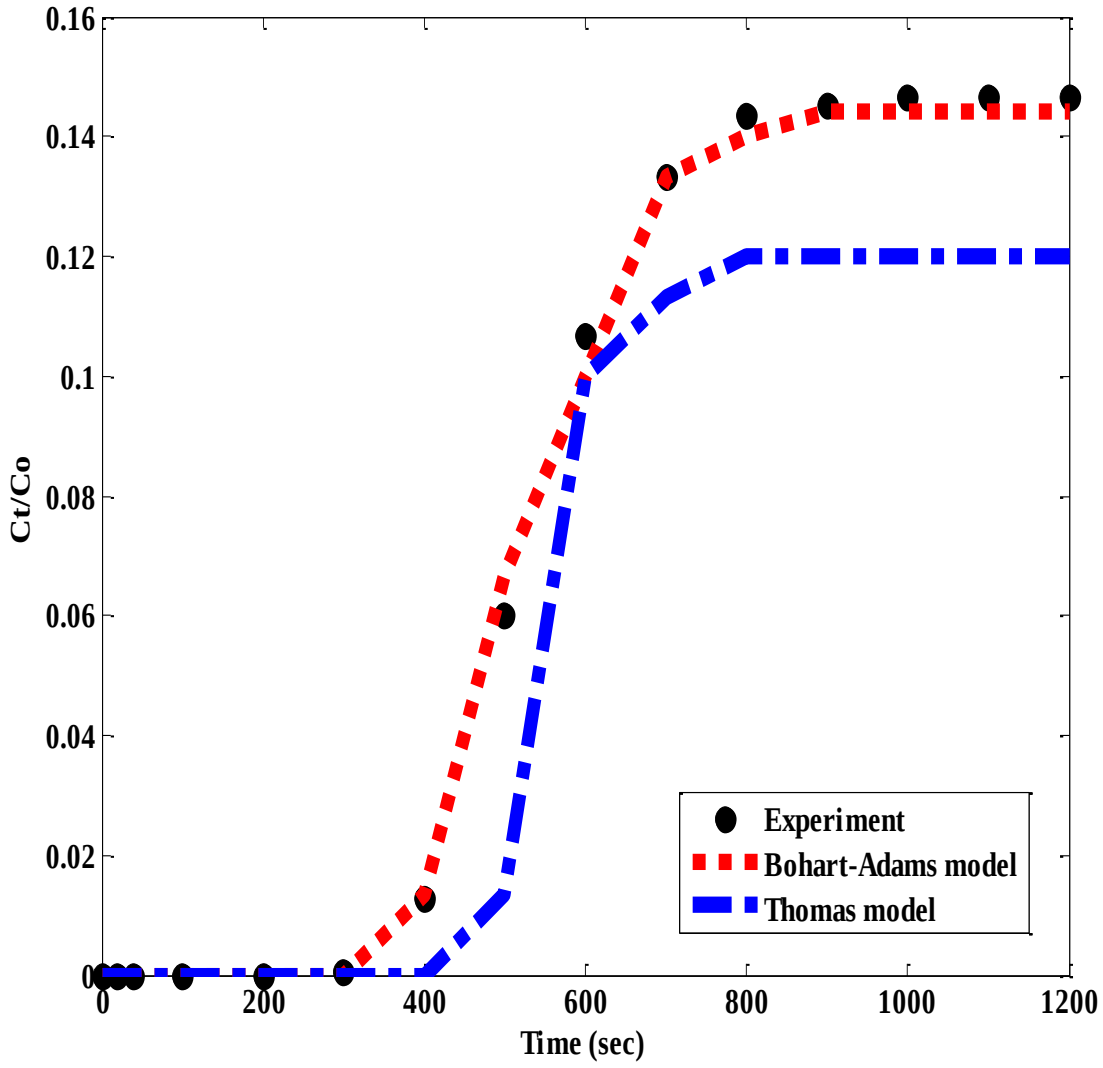
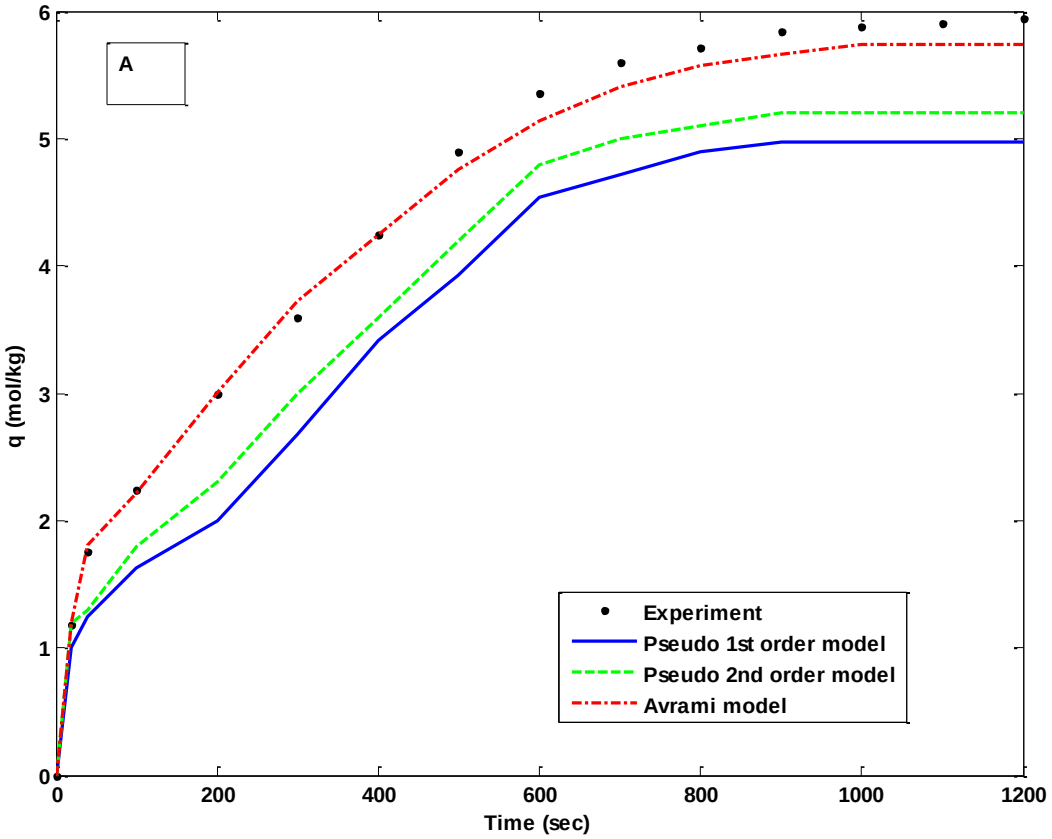
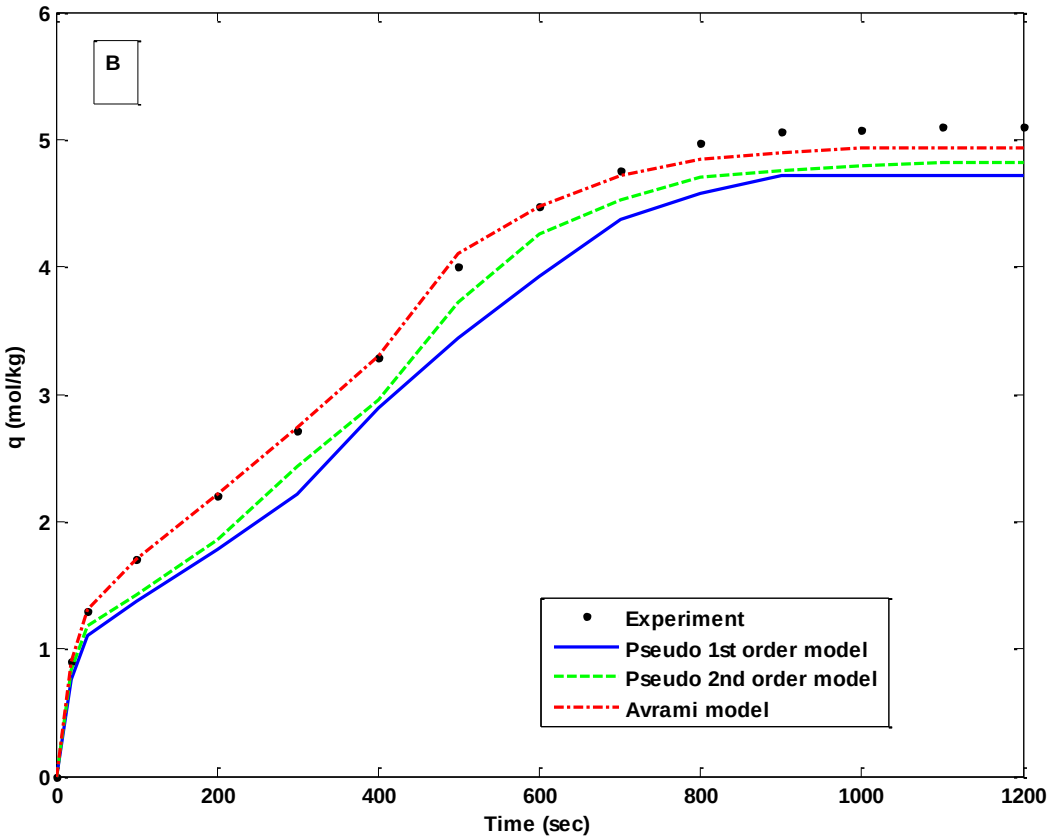


Figure 4.3 Experimental results versus model results. (Experimental conditions: 303 K, 2 bar)

Table 4.4 Kinetic model parameters for adsorption of CO_2 on polyaspartamide

Kinetic models	Parameters	303 K	318 K	333 K
Pseudo-first order model $q_t = q_e(1 - e^{-Kft})$	Kf (s^{-1})	3.2×10^{-2}	3.53×10^{-2}	3.92×10^{-2}
	Error (%)	1.33	5.27	2.8
	q_e (mol g^{-1})	4.97	4.72	4.37
Pseudo-second order model $q_t = \frac{q_e^2 K_s t}{1+q_e K_s t}$	Ks ($gmol^{-1}s^{-1}$)	2.24×10^{-2}	3.14×10^{-2}	4.42×10^{-2}
	Error (%)	8.81	3.88	2.33
	q_e (mol g^{-1})	5.2	4.82	4.4
Avrami model $q_t = q_e[1\text{-exp }(-(K_A t^{nA})]$	K_A (s^{-1})	3.99×10^{-2}	4.17×10^{-2}	4.31×10^{-2}
	Error (%)	2.38	2.22	1.55
	q_e (mol g^{-1})	5.74	4.94	4.45
	nA	1.76	1.46	1.38


A
q (mol/kg)
Time (sec)
0
1
2
3
4
5
6
0
200
400
600
800
1000
1200
Experiment
Pseudo 1st order model
Pseudo 2nd order model
Avrami model


B
q (mol/kg)
Time (sec)
Experiment
Pseudo 1st order model
Pseudo 2nd order model
Avrami model
0
1
2
3
4
5
6
0
200
400
600
800
1000
1200

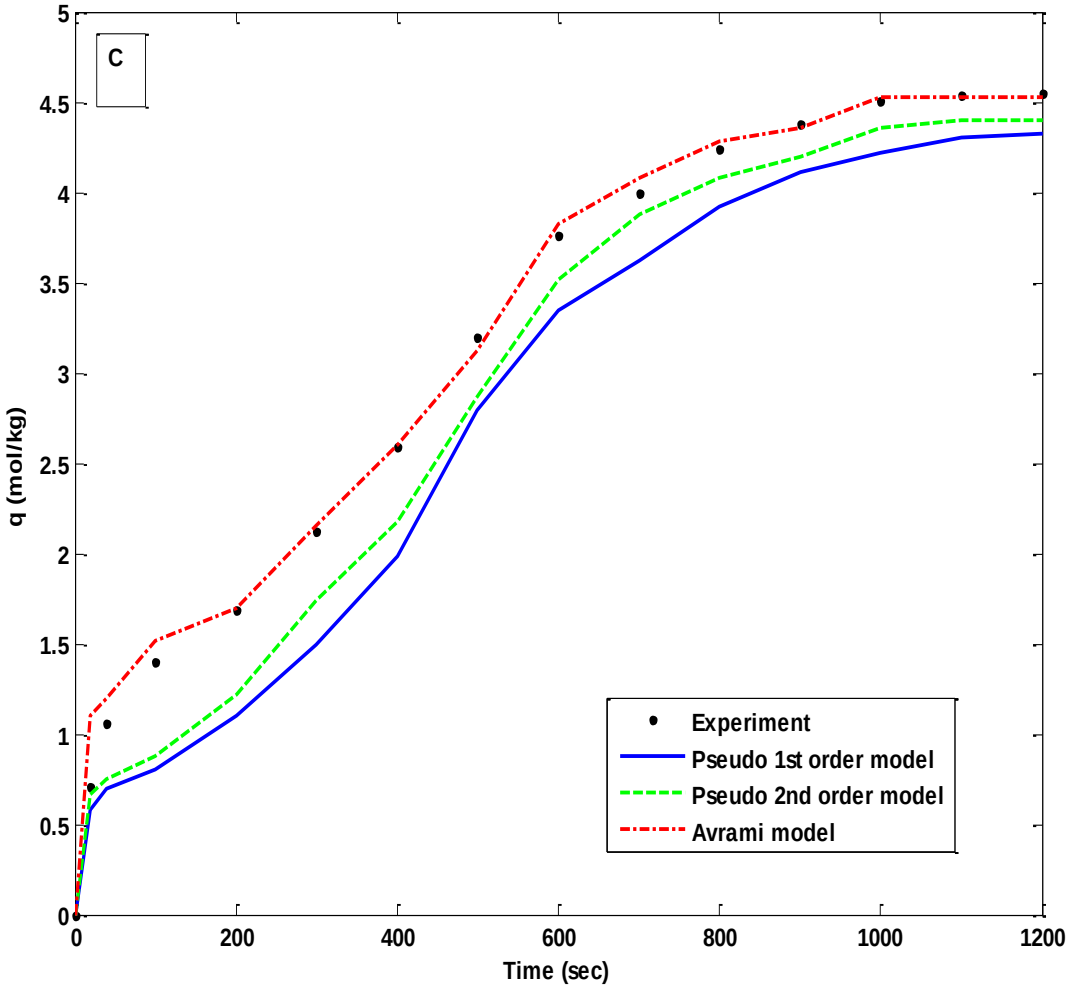


Figure 4.4 Experimental and predicted kinetics of adsorption of CO_2 onto polyaspartamide at (A) 303 K, 2 bar, (B) 318 K, 2 bar, (C) 333 K, 2 bar.

4.5 Summary

This chapter successfully investigated the adsorption behaviour of polyaspartamide as an adsorbent during post-combustion CO_2 capture using kinetics and breakthrough curves under different adsorption conditions and also attempted modelling these behaviours. Based on the outcome of this study in this chapter, it can be concluded that polyaspartamide is a promising adsorbent for post-combustion CO_2 capture. The breakthrough curve was successfully described using the Bohart-Adams model which could be attributed to the flexible assumptions of the Bohart-Adams model considered in this study. From the results of the Bohart-Adams model, it can be logically concluded that external mass transfer dominated the adsorption of CO_2 onto polyaspartamide. The shape of the breakthrough curve as predicted by

the model was in close agreement with experimental data and equilibrium was attained at various temperatures studied after 1000 seconds as depicted in Figure 4.1. The Avrami kinetic model consistently and successfully described the kinetics of adsorption of CO_2 onto polyaspartamide at all temperatures studied as shown in Figure 4.4. This simply implies that the adsorption of CO_2 onto polyaspartamide is more of a physisorption than chemisorption process (Physicochemical). Increasing the feed (i.e. CO_2) flow rate decreased the breakthrough time because faster flow rate decreases the retention time of the gas molecules on the adsorbent within the packed bed resulting in a decreased amount of CO_2 adsorbed by polyaspartamide. This simply means that, longer breakthrough times are required for a higher amount of CO_2 to be adsorbed by polyaspartamide which will subsequently result in a higher adsorption capacity.

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CHAPTER FIVE

Diffusion Mechanism and mass transfer limitation during the Adsorption of CO_2 on Polyaspartamide

5.1 Introduction

The adsorption of CO_2 onto most adsorbents used for CO_2 capture from a flue gas stream is significantly influenced by pore diffusion, external film diffusion, or by a combination of transport resistances which constitutes the rate-limiting step during the CO_2 adsorption process (Choy et al., 2004; Yoro and Sekoai, 2016). Different adsorption models have been developed in the past to investigate the mechanism of adsorption of different adsorbents (Qiu et al., 2009; Zhu et al., 2014). The resistance due to film diffusion is very important in any adsorption process (Guo et al., 2006). A number of gas-diffusion models with different levels of complexity have also been used in recent times to study the diffusion mechanism of different adsorbents (Marczewski et al., 2013; Whitaker, 1988). Ocampo-Pérez et al, (2013) used a homogenous surface diffusion model (HSDM) to predict the diffusion of gaseous molecules from the external surface of an adsorbent through the pore surface of the adsorbent. The model assumed that internal mass transfer occurs as a result of surface diffusion only with a negligible pore volume diffusion resistance (Baup et al., 2000). However, the limitation of this model was that it was used to describe only the surface diffusion coefficients in the adsorption process (Cook and Newcombe, 2008; Zhang et al., 2009). Viegas et al. (2014) combined the homogenous surface diffusion model (HSDM) with Boyd's diffusion model to estimate intra-particle diffusion coefficients in adsorption processes. The model was based on the assumption of external mass transfer and pore diffusion. Both group of researchers concluded that HSDM and Boyd's model of film diffusion can be used to describe the diffusion mechanism and rates controlling any gas-solid adsorption process. Currently, intra-particle diffusion model proposed by Boyd (Boyd et al., 1947) is a model widely used with kinetic data mainly to determine the rate limiting step controlling adsorption processes. Inter-particle diffusion model has also been used to study CO_2 adsorption mechanism on adsorbents at different adsorption temperatures and CO_2 partial pressures (Song et al., 2016).

In this study, diffusion mechanism and rate-limiting steps controlling the adsorption of CO_2 onto polyaspartamide in a CO_2/N_2 mixture was investigated using the Boyd's film model

alongside the inter-particle and intra-particle diffusion model at different operating pressures and adsorption temperatures. The usual adsorption process comprises of five steps; bulk diffusion, film diffusion, inter-particle diffusion, surface adsorption and intra-particle adsorption steps. But according to well established facts, surface adsorption is usually very fast and bulk diffusion is mostly negligible (Ho and Mckay, 1998; Ho, 2006). Therefore, this study only considered film diffusion, inter and intra-particle diffusion. The diffusion model developed by Boyd et al (1947) was adapted in this study to investigate whether the adsorption of CO_2 onto polyaspartamide was controlled by film or pore diffusion, while inter and intra-particle diffusion models were considered in this study in order to describe the actual rate-limiting step or mass transfer limitation controlling the adsorption of CO_2 onto polyaspartamide during post-combustion CO_2 capture.

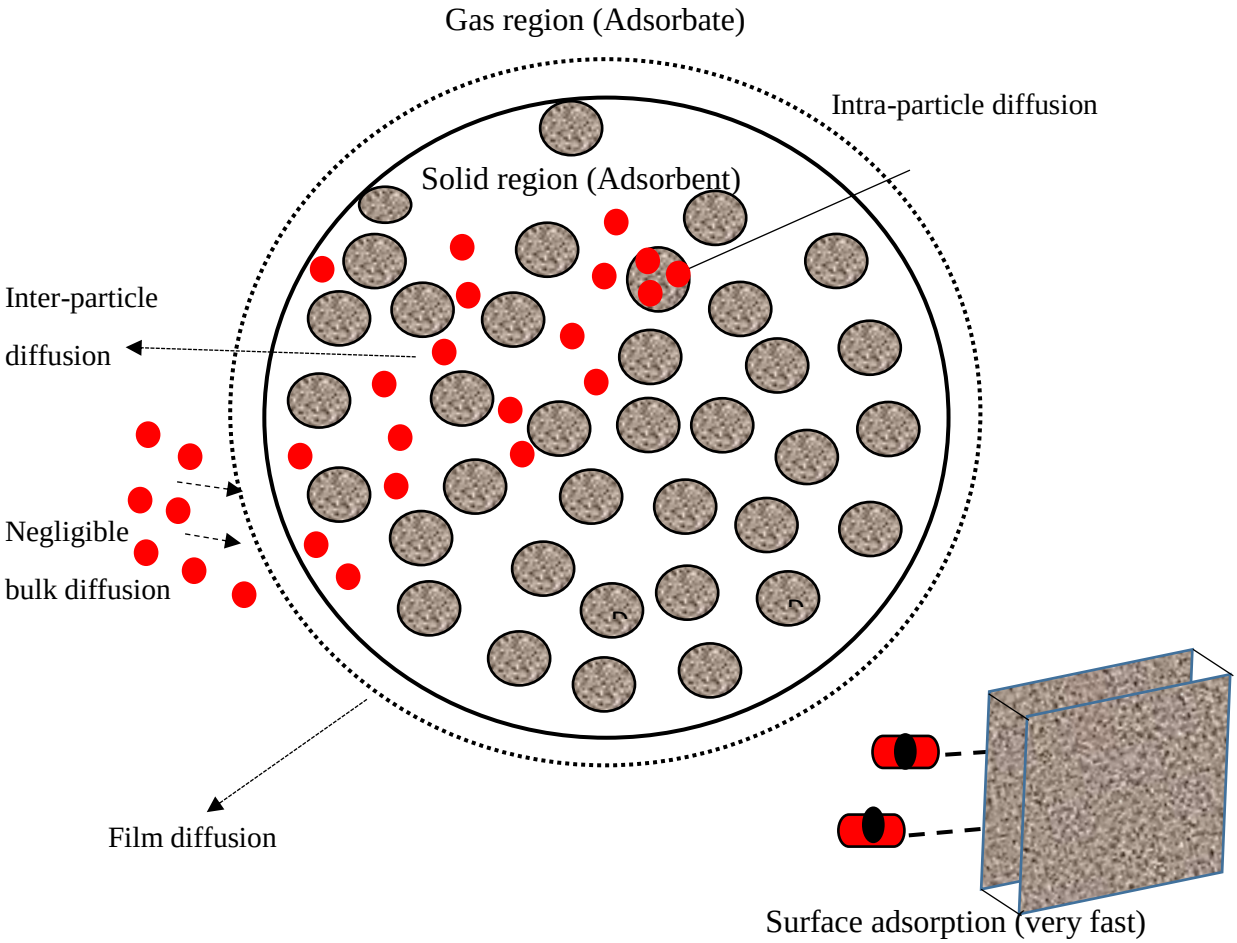


Figure 5.1 Adsorption mechanisms for CO_2 onto a solid sorbent (Adapted from Song *et al.*, 2016).

5.2 Theoretical background

5.2.1 Models

Several models based on film diffusion and rate-limiting steps have been reported in literature over the past decades (Crank, 1979; McKay and Al-Duri, 1990; Chen et al., 2001). The models selected in this study for investigating diffusion mechanism and rate-limiting steps assumed that external mass transfer and film diffusion govern the adsorption of CO_2 onto polyaspartamide. The aim was to apply a simple analytical solution to the adsorption of CO_2 from a CO_2/N_2 gas mixture onto polyaspartamide which is an amine-grafted polymer-based adsorbent. The models considered in this study were Boyd's diffusion model, interparticle and intra particle diffusion models adapted from previous studies reported by Viegas (Viegas et al., 2014), Boyd (Boyd et al., 1947) and Crank (Crank, 1979).The major assumptions made for the models considered in this chapter to investigate the diffusion mechanism of CO_2 onto polyaspartamide are summarized in Table 5.1;

Table 5.1 Models explored and assumptions made

Models Explored	Assumptions
Boyd's film diffusion model	1. External mass transfer controls the transport of gases through the surrounding of the stagnant film. 2. Mass transfer within the particle is attributed to diffusion within the pores of the adsorbent. 3. The adsorbate is attached to the surface of the adsorbent. 4. Mass transfer by film and surface diffusion is the only rate-controlling process.
Inter particle diffusion model	1.Mass transfer is as a result of diffusion between the pores of the adsorbent and molecules of the adsorbate
Intra particle diffusion model	1. External mass transfer is assumed to be due to diffusion within the pores of the adsorbent only

5.3 Diffusion Models

In 1947, Boyd developed mathematical models to study ion-exchange kinetics (Boyd et al., 1947). These models were found to be versatile with a wide range of applications in different adsorption studies to describe adsorption mechanisms and rate-limiting steps during a gas-solid adsorption process (Castillejos et al., 2010; Malash and El- Khaiary, 2010; El-Khaiary and Malash, 2011). The models also considered diffusion processes namely film and particle diffusion. The Boyd's film diffusion model is expressed in Equations (5.1) and (5.2) as adapted from a previous study (Alexander and Walter ,1997;Viegas et al., 2014).

$$B_t = -\ln \frac{\pi^2}{6} - \ln 1 - F_{(t)} \qquad \text{for } F_{(t)} > 0.85 \qquad (5.1)$$

$$B_t = \left(\sqrt{\pi} - \sqrt{\pi - \frac{\pi^2 F_{(t)}}{3}}\right)^2 \qquad \text{for } F_{(t)} \leq 0.85 \qquad (5.2)$$

Where B_t is the Biot number, $F_{(t)}$ is the fractional attainment of equilibrium and π = 3.142. The principle of film diffusion during the adsorption of CO_2 onto polyaspartamide was investigated using the model developed by Boyd et al (1947) while inter and intra particle diffusion models were used to describe the rate limiting steps. The molecular diffusion model as proposed by Boyd et al (1947) is expressed in Equations 5.3 and 5.4, respectively.

$$Ft = \frac{qt}{qe} = 1 - \frac{6}{\pi^2} \text{ x } \sum_{n=1}^{\infty} X\, e^{-n^2\, X\, B} \qquad (5.3)$$

$$\text{B} = \frac{\pi^2 \text{x} D_i}{R^2} \qquad (5.4)$$

Where q_e is the equilibrium concentration of CO_2 adsorbed by the adsorbent and qt is the final concentration of CO_2 at a particular time (t), B is the Boyd number D_i is the effective intraparticle diffusion coefficient.

5.4 Materials and Methods

5.4.1 Materials

The materials used in this study are polyaspartamide and flue gas source with composition of 15% CO_2 and 85% N_2 which have been extensively discussed in chapter 3 of this dissertation.

5.4.2 Methods

A detailed experimental method has been explained in chapter 3 of this dissertation. But for the study contained in this chapter, a continuous adsorption experiment was conducted in a laboratory-scale packed bed adsorption column at isothermal conditions (303, 318 and 333 K) and constant operating pressure of 2 bars. Data obtained from the experimental study were imputed into the Boyd's, inter-particle as well as intra particle diffusion models in order to adequately investigate the adsorption mechanism and rate limiting steps involved in the CO_2 adsorption process. Model parameters were solved in MATLAB R2014a. The result that appears to be in a closer agreement with the assertions of the diffusion models was considered as the mechanism and rate-limiting step controlling the adsorption of CO_2 onto polyaspartamide.

5.5 Results and Discussion

5.5.1 Boyd's Film Diffusion Model Results

One of the most important factor to consider in any adsorption mechanism study is film diffusion (Carta and Lewus, 2000; Huang et al., 2015). The equilibrium concentration (qe) in this study was estimated by the Freundlich isotherm. The expressions from film diffusion model proposed by Boyd et al in 1947 as represented in Equations (5.1) and (5.2) were used to investigate whether the adsorption of CO_2 onto the amine-grafted polyaspartamide is controlled by film or pore diffusion. Boyd et al (1947) in their film diffusion model for gas-solid adsorption suggested that if the plot of Bt against time is non-linear, the process is suspected to be controlled by film diffusion. Figures. 5.2 and 5.3 show a non-linear Boyd's diffusion model plots at different CO_2 partial pressures and adsorption temperatures respectively. The plots of Bt against time at different partial pressures and constant temperature was non-linear and the plot at different adsorption temperatures and constant pressure was more of a scattered plot. The scattered plots could be attributed to the magnified fluctuation of $\frac{qt}{qe}$ caused by the logarithmic term in the model.

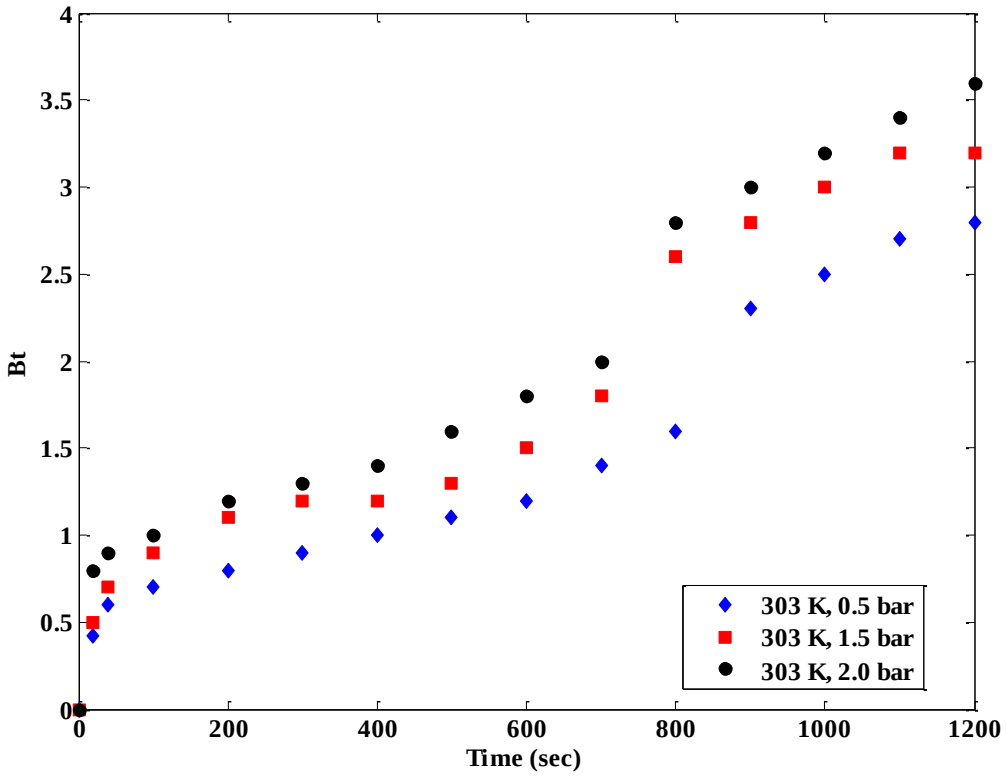


Figure 5.2. Boyd's film diffusion model for CO_2 adsorption on polyaspartamide at different pressure.

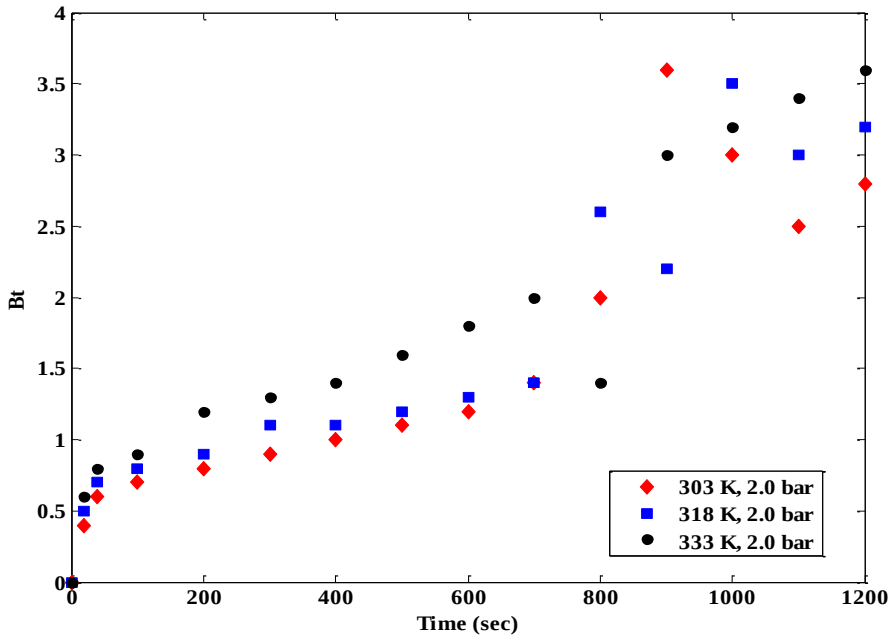


Figure 5.3 Boyd's film diffusion model for CO_2 adsorption onto polyaspartamide at different adsorption temperature and constant pressure.

5.5.2 Inter particle diffusion model

Inter-particle diffusion model was adapted from a similar study to describe the CO_2 adsorption mechanism of polyaspartamide at different adsorption temperatures and CO_2 partial pressures in order to ascertain the actual rate-limiting step controlling the adsorption of CO_2 onto polyaspartamide. According to the inter-particle diffusion model, a plot of ln (1-q_t/q_e) against time is expected to be linear having an intercept of ln $6/\pi^2$ which when simplified is given as -0.498 (Song et al., 2016). From this study, the intercept of a plot of ln (1- q_t/q_e) versus time as depicted in Figures 5.4 and 5.5 were -0.7, -0.8 and -0.9 at different temperatures of 333, 303 and 318 K respectively at a constant pressure of 2 bar as well as -0.4, -0.55 and -0.6 at a pressure of 0.5, 1.5 and 2 bar respectively and a constant temperature of 303 K. According to the results obtained from Figures 5.4 and 5.5, the intercepts were not in agreement with the value of ln $6/\pi^2$ as there was a slight deviation. This however indicates a violation of the assertion that inter-particle diffusion model is the rate-limiting step controlling the adsorption mechanism of CO_2 onto polyaspartamide. This invariably means that there must be another mechanism governing the adsorption of CO_2 onto polyaspartamide.

Since the fractional adsorption capacity is greater than 0.7, Equation (5.3) can be re-written as:

$$\frac{qt}{qe} = 1 - \frac{6}{\pi^2}\exp\left(-\frac{\pi^2 Dct}{r_p^2}\right) \quad (5.4)$$

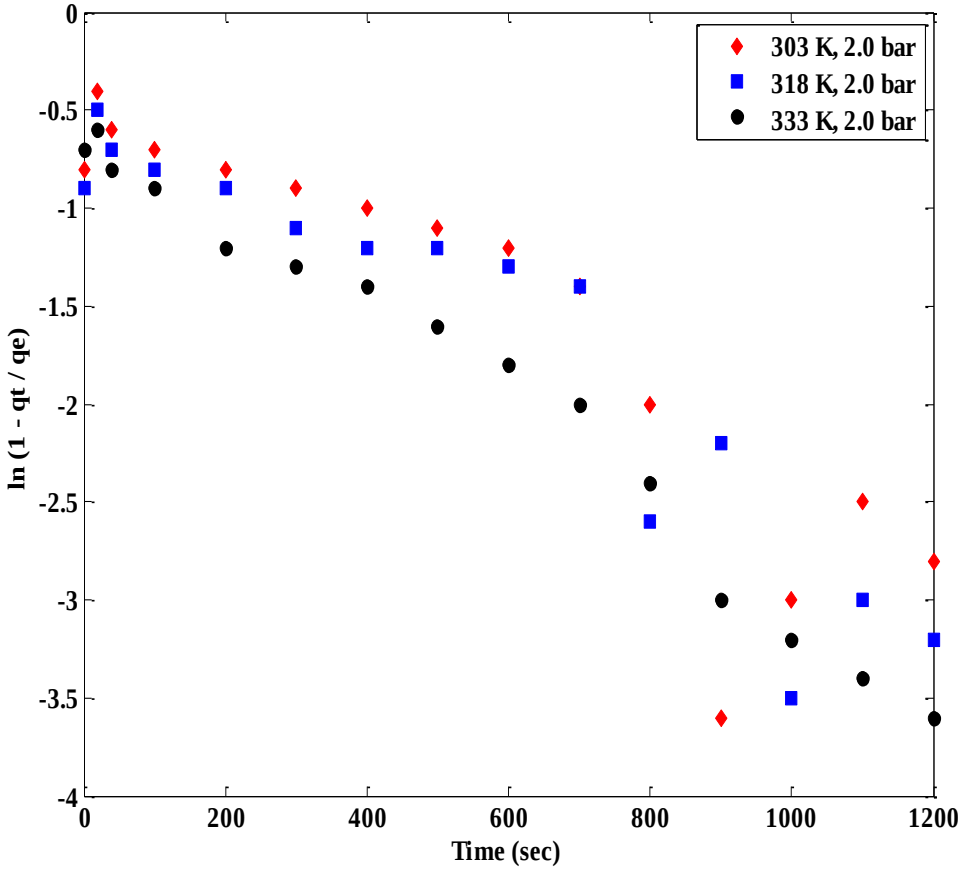


Figure 5.4. Inter-particle diffusion model plots for CO_2 adsorption on polyaspartamide at different adsorption temperature and constant pressure.

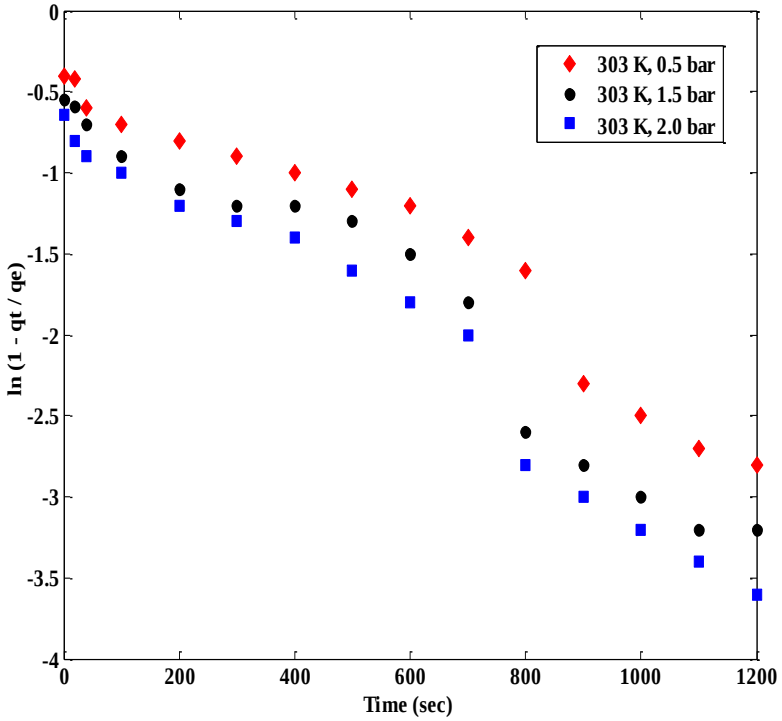


Figure 5.5 Inter-particle diffusion model plots for CO_2 adsorption on polyaspartamide at different CO_2 partial pressures.

5.5.3 Intra-particle diffusion model

Since the inter particle diffusion model could not adequately describe the rate limiting step earlier in this study, the intra-particle diffusion model was then adapted from previous studies (Song et al., 2016) to analyse the CO_2 adsorption process in order to make a logical conclusion on the rate-limiting step governing the adsorption process in this study. According to the intra-particle diffusion model reported in literature (Song et al., 2016), a plot of qt against $t^{1/2}$ is expected to be multilinear. The multilinear nature of the intra particle diffusion model plots depicted in this study indicate that apart from the intra-particle resistance, other rate-limiting steps also have a role to play on the adsorption of CO_2 onto polyaspartamide. Intra-particle resistance is responsible for the sluggish adsorption step after breakthrough has been attained during the adsorption of CO_2 onto polyaspartamide. According to the results depicted in Figures 5.6 and 5.7, the adsorption curves obtained at various adsorption temperatures and CO_2 partial pressures showed twin linearity. The twin linearity displayed by the curves in Figures 5.6 and 5.7 indicate that there are two rate-limiting steps controlling the adsorption of CO_2 onto the adsorbent. Based on the outcomes from this study, it could be inferred that film diffusion resistance and resistance due to intra-particle diffusion are the

rate-limiting steps governing the adsorption of CO_2 onto polyaspartamide. The intra particle diffusion model represents a simple approximation of diffusion kinetics and is expressed as:

$$q_t = K_{id} t^{0.5} + C \quad (5.5)$$

Where q_t is the amount of CO_2 adsorbed, t is time and K_{id} is an intra-particle kinetic parameter.

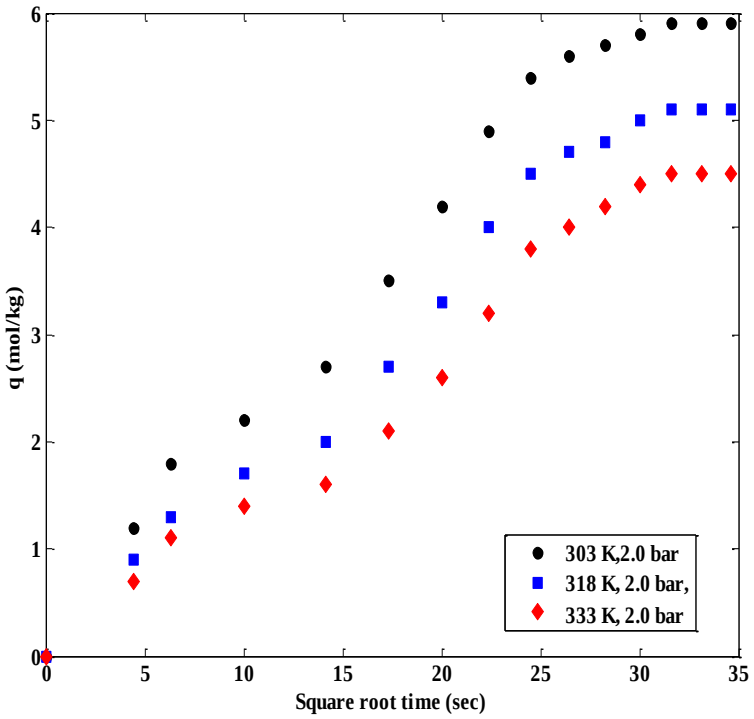


Figure 5.6 Intra-particle diffusion model plots for CO_2 adsorption on polyaspartamide at different adsorption temperatures.

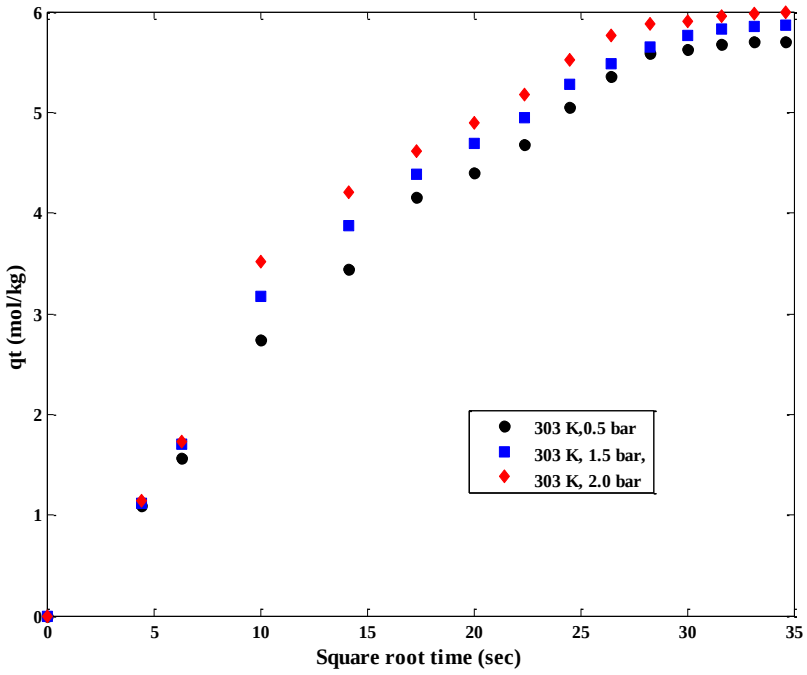


Figure 5.7 Intra-particle diffusion model plots for CO_2 adsorption on polyaspartamide at different CO_2 partial pressures.

5.6 Summary

The mechanism of diffusion and rate limiting steps controlling the adsorption of CO_2 onto a novel polyaspartamide material was successfully investigated using Boyd's, inter-particle and intra-particle diffusion models. Based on the outcome of this study, Boyd's film diffusion model accurately confirmed that the adsorption of CO_2 onto polyaspartamide is controlled by film diffusion. The intra-particle diffusion model also confirmed that intra-particle diffusion and film diffusion resistance is the rate-limiting step controlling the adsorption of CO_2 onto polyaspartamide during the capture of CO_2 from a CO_2/N_2 mixture. This means that, external mass transfer during the adsorption process was due to diffusion within the pores of the adsorbent (polyaspartamide) only. Finally, it can be concluded that film diffusion was responsible for the very rapid initial stage observed during CO_2 uptake while the latter sluggish stage was as a result of intra-particle diffusion resistance caused by the abundant narrow pores on the novel polyaspartamide material which mitigated the diffusion rate of CO_2.

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CHAPTER SIX

Parametric Effect on the CO_2 Adsorption Performance of Polyaspartamide (PAA)

6.1 Introduction

The composition of flue gas streams from a typical power plant is 68-75% N_2, 10-15% CO_2, 5-10% H_2O and 2-5% O_2 with traces of NOx and SOx. Conventionally, the wet flue gas is pre-treated and dried to reduce its moisture content (Xu et al., 2011; Ntiamoah et al., 2016). Although the conventional approach of pre-treating and drying flue gas before capturing its CO_2 content seem to be a viable option which is widely embraced industrially. However, this option increases the overall cost of the CO_2 capture process. (Zhang et al., 2009; Sekoai and Yoro, 2016). Before designing an adsorption process, selecting an appropriate adsorbent with high level of hydrophobicity and working capacity as well as a strong desorption capability is the key to an efficient and effective CO_2 capture (Yoro and Sekoai, 2016). A wide variety of adsorbents such as synthetic zeolites (Siriwardane et al., 2005; Samanta et al., 2012; Younas et al., 2016), activated carbon(Siriwardane et al., 2001; Lu et al., 2008; Pellerano et al., 2009;), carbon molecular sieves (Carruthers et al., 2012), silica and metal oxides (Wan et al., 2014), metal organic frameworks (Liang et al., 2009; Zhao et al., 2009) have been developed and studied for CO_2 capture under dry and wet conditions. Adsorbents like zeolites and carbon molecular sieves exhibit high level of hydrophilicity and moisture content hardly gets desorbed from their pores (Li et al., 2009; Songolzadeh et al., 2014). For instance, adsorbents determine the CO_2 capture performance in the vacuum swing adsorption technology (Chaffee et al., 2007). The key elements for a good adsorbent in CO_2 capture technology among other elements are, rapid adsorption/desorption kinetics, moisture resistance, stable adsorption capacity after repeated cycles and adequate mechanical strength of the particles (Yang, 2003). Most of these key elements for a good adsorbent have been studied and reported in literature (Wang et al., 2010; Ngoy et al., 2014; Chitsiga et al., 2016). But investigating the numerical effect of moisture and operating parameters such as pressure, temperature and flow rates on the adsorption capacity of polyaspartamide during post combustion CO_2 capture is not adequately reported.

Against this background, this study investigated the parametric effect of moisture and the key operating variables on the adsorption behaviour of polyaspartamide during post-combustion CO_2 capture. Polyaspartamide is a novel amine grafted polymer-based adsorbent obtained

when polysuccinimide reacts with Ethylene diamine (EDA). This material has proven to be a potential adsorbent for post-combustion CO_2 capture due to its high CO_2 selectivity, high adsorption capacity and excellent thermal stability (Ngoy et al., 2014).

The effect of moisture on adsorbents during CO_2 capture needs to be studied in-depth because most flue gases from power plants contain moisture (Zhang et al., 2014) . The moisture occupies the pores of the adsorbents because most adsorbents have a higher affinity for water or moisture than CO_2. Therefore, If polyaspartamide must be used as an adsorbent for CO_2 capture from flue gas stream of power plants, then there is need to understand the effect of moisture on the performance of such adsorbent during the CO_2 capture process (Li et al., 2009). The effect of moisture on the adsorption capacity of an adsorbent during CO_2 capture could be advantageous or detrimental (Marx et al., 2013). Previous studies have speculated that amine-rich polymer-based adsorbents exhibit a high tolerance level for moisture (Chou and Chiou, 1997; Hefti et al., 2014). The effects of moisture on the performance of adsorbents for CO_2 capture can be investigated using experimental or modelling approach (Chou and Chiou, 1997). Experimentally, the effect of moisture on the CO_2 adsorption capacity of an adsorbent can be investigated by installing a moisture saturator on a fluidized bed in order to generate a stream of moisture that would be injected into the flue gas stream or by first getting the adsorbent wet with moisture before feeding it to the packed bed during the CO_2 capture experiment. Alternatively, mathematical models can be used to investigate the effects of moisture on the adsorption capacity of an adsorbent theoretically and numerically by incorporating a moisture parameter such as vapour pressure or humidity parameter into a model that was initially used to describe the adsorption capacity of similar adsorbents using dry flue gas mixtures (Qi et al., 2000; Shafeeyan et al., 2014). Effect of vapor pressure on the adsorption capacity of specific adsorbents was described previously by the popular Langmuir, Freundlich, and Dubinin-Radushkevich equations as reported in previous studies (Chou and Chiou, 1997; Qi et al., 2000; Drage et al., 2007; Veneman et al., 2014). This approach was adapted in this study. The effect of temperature on the adsorption behaviour of polyaspartamide was described by the Langmuir isotherm.

Another factor that has effect on the adsorption capacity of any adsorbent is the operating conditions under which the said adsorbent is used (Wang et al., 2010; Alhwaige et al., 2016; Titinchi et al., 2014;). Understanding the effect of operating conditions on the performance of polyaspartamide during CO_2 capture is very important. Pressure, temperature and gas

flowrate-dependency of the adsorption capacity of polyaspartamide during the adsorption of CO_2 need to be fully evaluated before a logical conclusion on the behaviour of this adsorbent can be made. On this note, this chapter seeks to investigate the effects of moisture on the adsorption capacity of polyaspartamide during post combustion CO_2 capture using mathematical modelling approach by incorporating a vapour pressure parameter onto an existing gas-solid adsorption model and also study the effects of operating conditions such as temperature, pressure, and flow rate on the adsorption capacity of polyaspartamide during post-combustion CO_2 capture.

6.2 Materials and methods

6.2.1 Materials

Polyaspartamide material was the adsorbent considered in this study. Its synthesis and characterization procedure was extensively described in our previous study (Ngoy et al., 2014; Chitsiga et al., 2016) as reported in previous chapters. Details about the materials used in this study have been extensively discussed in chapter 3 of this dissertation (see chapter 3, point 3.4).

6.2.2 Methods

The parametric effect of moisture and operating variables on the adsorption capacity of polyaspartamide was investigated using an experimental study and modelling approach. Experimental data from our previously conducted experiment was fitted into mathematical models adapted from a similar study reported in literature (Chou and Chiou, 1997). The effect of pressure, temperature and gas flowrate on polyaspartamide was studied using the Bohart-Adam's model. A model adapted from a study conducted by Chou and Chiou, (1997) was used to describe the effect of moisture on the adsorption capacity of polyaspartamide. Within the experimental conditions, the adsorption capacities of polyaspartamide for CO_2 both humid and dry air streams were related to the operating pressure.

6.3 Experimental and Modelling

Experiments were first carried out to determine the adsorption capacity of polyaspartamide under dry conditions in a laboratory-scale packed bed adsorption column. The experiment was conducted at temperatures of 303, 318 and 333 K, pressure range of 1-2 bars. 0.1 g polyaspartamide was fed into the packed bed and pure N_2 was used to purge the adsorption

column at 373 K for 20 minutes (1200 seconds) to get rid of impurities. The temperature was lowered to 333, 318 and 303 K and concentration of CO_2 was obtained from the CO_2 gas analyser. The dry feed gas (15% CO_2, 85% N_2) was then fed into the adsorption column while by-passing the reactor and the initial concentration of CO_2 were obtained repeatedly at different temperatures. Adsorption capacity of the material was then calculated from the experimental data obtained. Details of the experimental procedure are provided in Chapter 3 of this dissertation.

An existing gas-solid adsorption model with vapour pressure parameter incorporated in it adapted from a previous study by Chou and Chiou (1997) was adapted in this study. The model was modified to suit the assumptions in this study and experimental data was imputed into the model at wet conditions. The adsorption capacities of polyaspartamide under wet and dry conditions were obtained and the results were compared.

6.4 Results and Discussion

The parametric effect of temperature, pressure and gas flow rates during the adsorption of CO_2 onto polyaspartamide under dry conditions as well as the effect of moisture on the adsorption capacity of polyaspartamide are presented and discussed in the following sections.

6.4.1 Effect of Moisture

In real-life situation, flue gas from power plants always contains some percentage of moisture. The moisture content of flue gases can have a negligible, detrimental or incremental effect on the adsorption capacity of solid sorbents during CO_2 capture. It is therefore imperative to understand the effect of moisture on the adsorption capacity of polyaspartamide which is an emerging adsorbent for post-combustion CO_2 capture. Most amine–rich adsorbents have shown a high level of tolerance for moisture unlike other physical adsorbents. A bicarbonate compound is formed when CO_2 reacts with a primary amine group under wet conditions and carbamate is formed under dry conditions when CO_2 reacts with primary amine groups according to the following chemical schemes (Stowe et al., 2015):

$$RNH_2 + CO_2 + H_2O \rightleftharpoons RNH_3^+HCO_3^- \quad \text{(bicarbonate)} \qquad (6.1)$$

$$2(RNH_2) + CO_2 \rightleftharpoons RNHCO_2^-RNH_3^+ \quad \text{(carbamate)} \qquad (6.2)$$

This study employed a simple mathematical model adapted from the Polanyi adsorption potential theory to predict the effect of moisture on the CO_2 adsorption capacity of polyaspartamide.

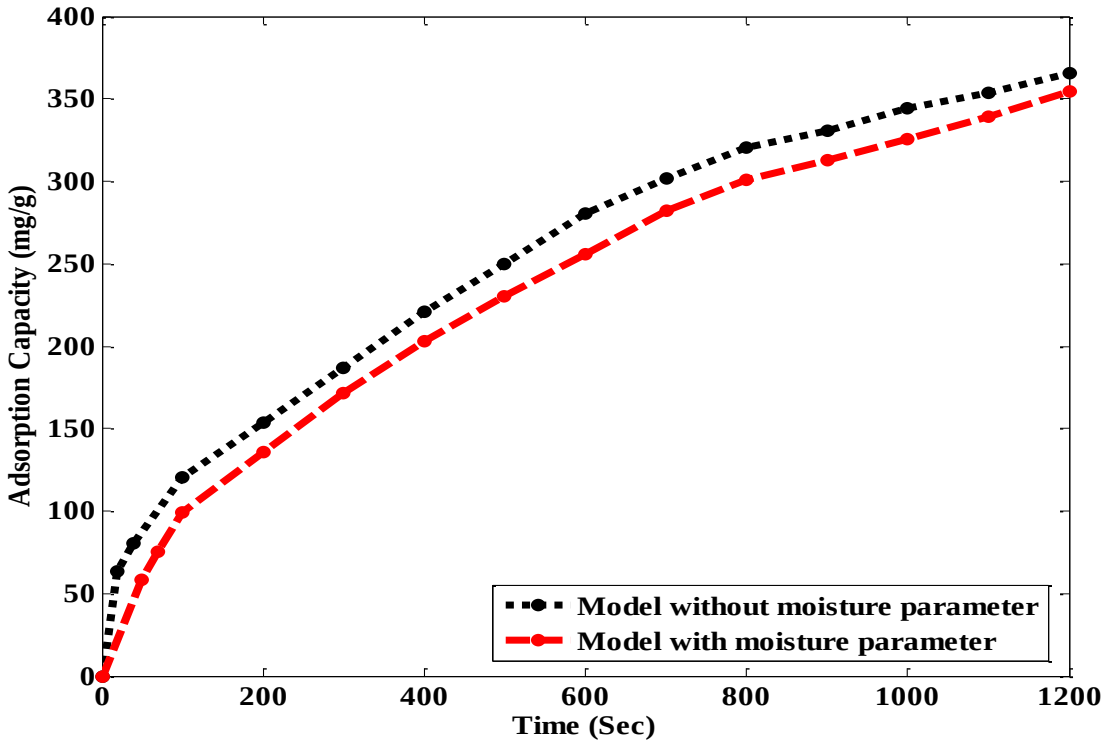


Figure 6.1 Theoretical effect of moisture on the CO_2 adsorption behaviour of polyaspartamide.

The result presented in Figure 6.1 depicts that the model predicted an adsorption capacity of 365.4 $mgCO_2/g$ adsorbent and 354.1 $mgCO_2/g$ adsorbent under dry conditions and wet conditions respectively. This shows only a negligible decrease in the adsorption capacity of polyaspartamide due to the presence of moisture. This slight decrease could be attributed to the fact that some moisture molecule did not completely react with amine to form bicarbonate instead; they filled the pores of polyaspartamide and thus reduced the pore spaces for CO_2 adsorption. Adsorption of gases as a single component on an adsorbent was quantified using the Dubinin-Raduskervich equation which follows that:

$$q_a = \rho_a W_a \exp\left[-K_a \left(\frac{RTlnPa_s}{P_a}\right)^2\right] \quad (6.3)$$

Where $V_{a,\,max} \geq V_{w,\,max}$, $\rho_a = density\ of\ CO_2$, W_a= limiting adsorption volume for CO_2. D-R isotherm parameter mol/kJ^2. Pa_s = Saturated vapor pressure of CO_2 and P_a = vapor pressure in the presence of moisture and K_a molar volume of the gas (CO_2).

6.4.2 Effect of Temperature

The effect of temperature on the adsorption of CO_2 onto polyaspartamide was studied by fitting experimental data to a standard adsorption isotherm model like the Langmuir adsorption model. The Langmuir isotherm equation is represented in Equation (6.4):

$$q = \frac{q_{mKP_{CO2}}}{1+KP_{CO2}} \tag{6.4}$$

Where q is the amount of CO_2 adsorbed at the pressure P, q_m is the amount of CO_2 adsorbed with monolayer coverage and K is the Langmuir constant. The adsorption isotherm exhibited a monolayer adsorption mechanism. It was also observed that the isotherms studied displayed a common behaviour notwithstanding the temperature as depicted in Figure 6.2. This is because the amount of CO_2 adsorbed by the adsorbent increased rapidly with a decrease in temperature and an increase in pressure and then stabilizes afterwards. It also revealed the behaviour of polyaspartamide by showing the effect of temperature on the amount of CO_2 that could be adsorbed as well as the adsorption capacity. A decrease in the adsorption temperature led to an increase in the amount of CO_2 adsorbed by polyaspartamide. The adsorption isotherm presented in this chapter showed the effect of temperature on the amount of CO_2 adsorbed by polyaspartamide. In this dissertation, the maximum amount of CO_2 adsorbed on polyaspartamide was 5.9 mol of CO_2 on every kilogram of adsorbent at 303 K while a 4.5 mol of CO_2 per kilogram of adsorbent was adsorbed by polyaspartamide at 333 K, constant pressure of 2 bar and gas inlet flow rate of 2.5 ml/s as depicted by the adsorption isotherm curves in Figure 6.2

The amounts of CO_2 adsorbed on polyaspartamide were 5.9, 4.8 and 4.1 mol CO_2/kg adsorbent for adsorption temperatures of 303, 318 and 333 K respectively. This simply implies that the ideal temperature for the adsorption of CO_2 onto polyaspartamide was determined at 303 K in this study as it resulted in giving the result with the highest amount of CO_2 adsorbed. Values for the Langmuir isotherm parameters obtained in this study were compared with literature values and presented in Table 6.1. The one reported in literature was

conducted at a lower tempoerature compared to this study, hence the slight discrepiancies in results.

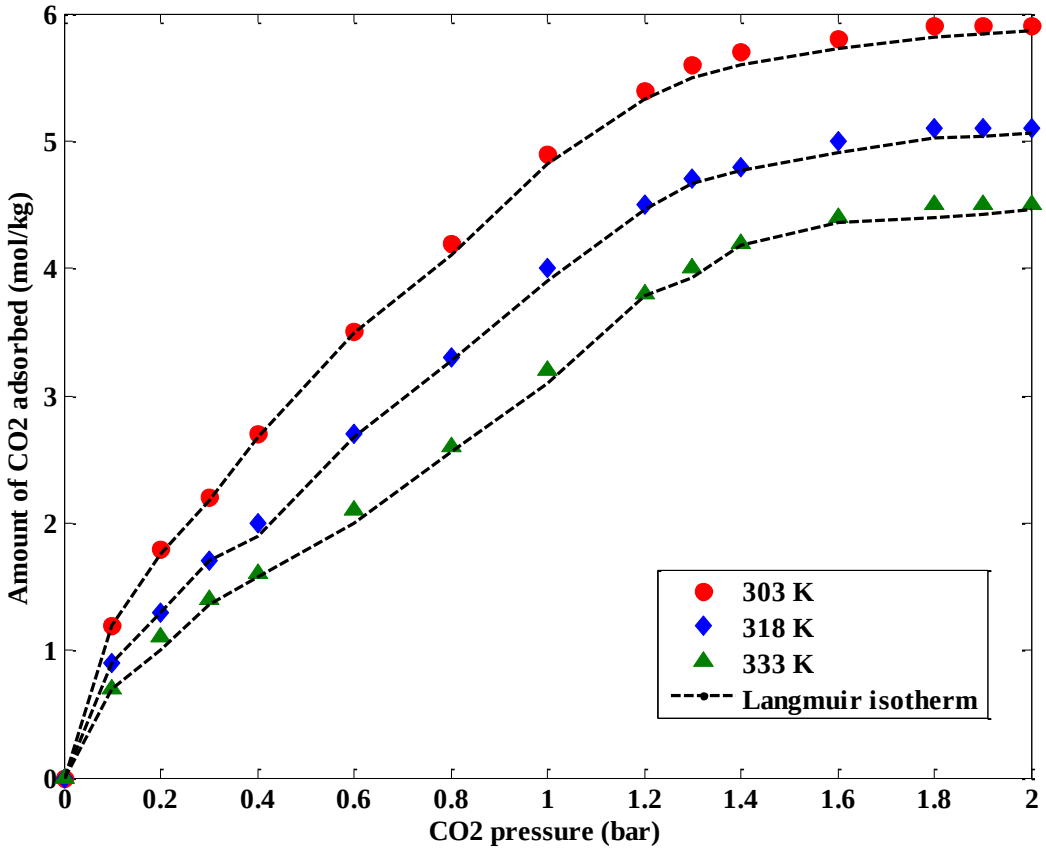


Figure 6.2 CO_2 adsorption isotherms of polyaspartamide at various temperatures (Experimental Vs Langmuir Isotherm).

Table 6.1 Parameters for the Langmuir isotherm Compared with literature

T (K)	q_m (mol/kg)	K (bar^{-1})	References
288	41.31	0.026	Khalili et al (2016)
298	30.81	0.020	Khalili et al (2016)
308	28.79	0.018	Khalili et al (2016)
303	5.82	0.017	This study
318	4.641	0.012	This study
333	3.785	0.005	This study

6.4.3 Effect of Operating Pressure

Pressure is an important parameter for measuring the behaviour and adsorption capacity of solid sorbents. According to the results presented in Figure 6.3, at higher operating pressures, the CO_2 adsorption capacity of polyaspartamide increased and at lower operating pressures resulted in a decrease in the adsorption capacity of polyaspartamide at the same operating temperature. The CO_2 adsorption capacity of polyaspartamide were 349, 333 and 317 $mgCO_2/g$ adsorbent at an operating pressure of 2, 1.5 and 1 bar, respectively. The adsorption capacities were obtained in a packed bed adsorption column at an operating temperature of 303 K as depicted in Figure 6.3. The maximum adsorption capacity for polyaspartamide reported in this study (349 $mgCO_2/g$) which was obtained in a packed bed adsorption column using a balanced 15% CO_2 and 85% N_2 source was far higher than that reported by Chitsiga et al. (2016) (44 $mgCO_2/g$) using a 100% CO_2 source in a thermogravimetric analyser (TGA) under the same operating conditions with this study. This is because there was a closer contact between the adsorbent (Polyaspartamide) and the gas in the packed bed than in the thermogravimetric analyser.

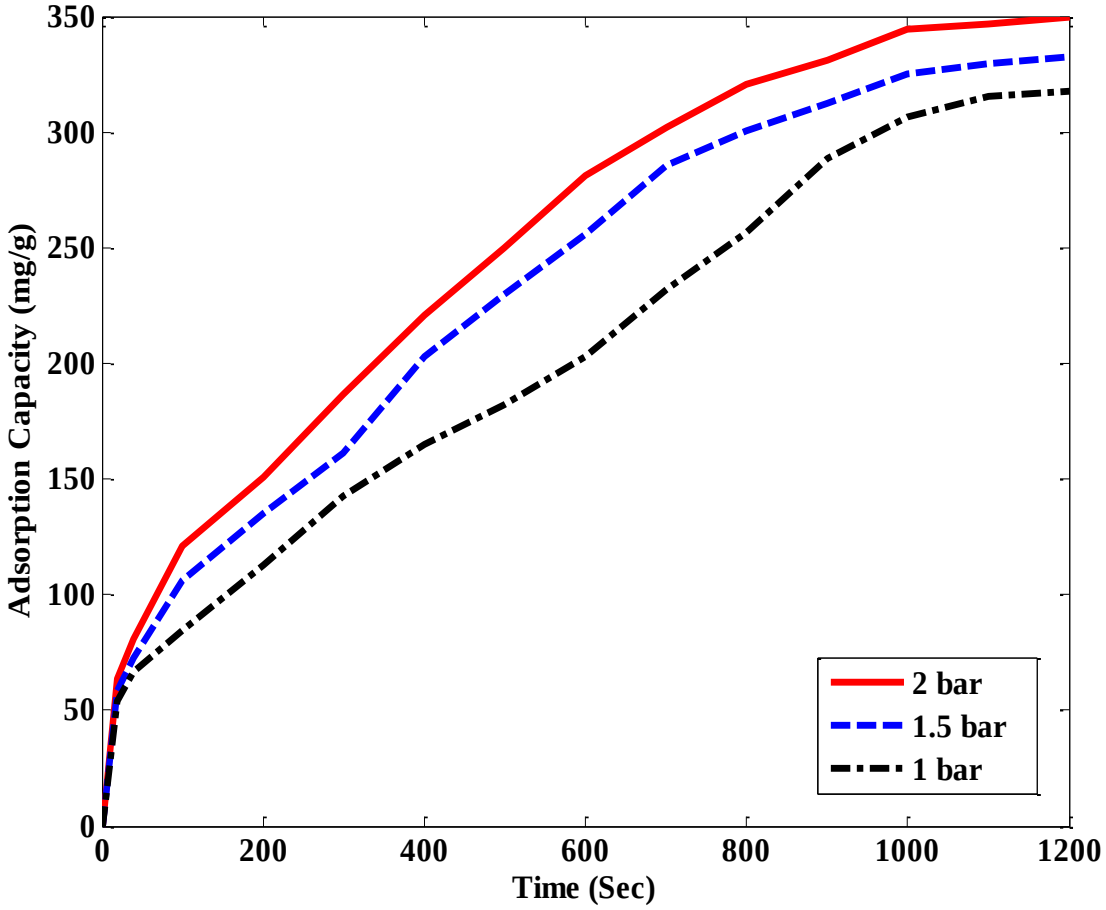


Figure 6.3 Effect of operating pressure on the adsorption capacity of polyaspartamide

6.4.4 Effect of inlet gas flow rate

The results for the adsorption of CO_2 onto polyaspartamide obtained under different inlet flowrates are presented in Figure 6.4. It was observed that decreasing the inlet flow rate of the gas increases the contact time and improves mass transfer between CO_2 and polyaspartamide. That is, lower flow rates increase the retention time of the CO_2 molecules on polyaspartamide within the packed bed adsorption column resulting in the high amount of CO_2 adsorbed. Longer residence times are required for a higher amount of CO_2 to be adsorbed and entrapped in the pores of polyaspartamide. As a result of the aforementioned reasons, the maximum amount of CO_2 adsorbed by polyaspartamide at different flow rates of 1.0, 1.5 and 2.5 ml/s CO_2 were 7.84, 6.5 and 5.9 mmol CO_2/g of adsorbent as depicted in Figure 6.4.

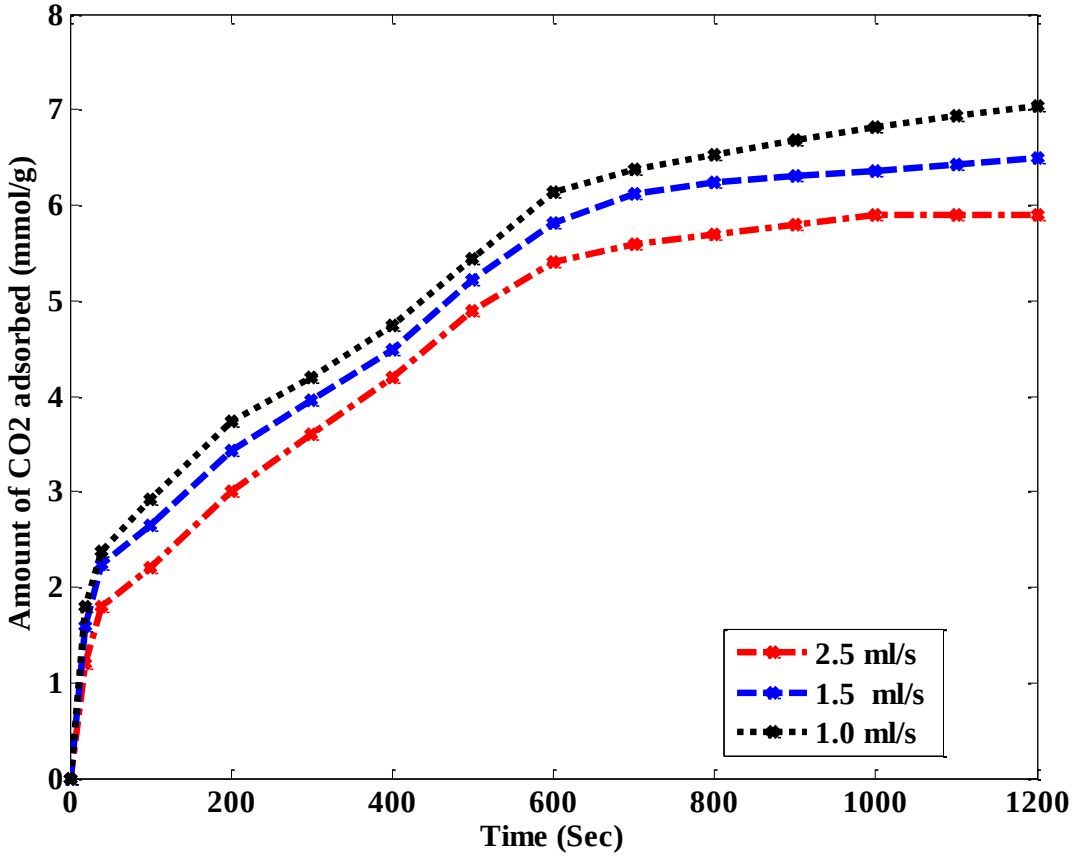


Figure 6.4 Effect of flow rates on the amount of CO_2 adsorbed onto polyaspartamide.

6.5 Summary

This study experimentally examined the parametric effect of temperature, operating pressure and gas flowrate on the adsorption capacity of polyaspartamide during CO_2 capture in a packed bed adsorption column. Higher amounts of CO_2 were adsorbed at lower temperatures and higher operating pressure while lower flowrates had an incremental effect on the adsorption capacity of polyaspartamide as seen in the results presented. Effect of moisture was numerically and theoretically studied using mathematical models. It was confirmed that the presence of moisture had a negligible decrease on the adsorption capacity of polyaspartamide which is common with most amine-rich polymeric sorbents. This numerical approach is more straightforward and better suited than the original graphical technique commonly used for dynamic simulation of activated carbon adsorbers.

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CHAPTER SEVEN

Mathematical modelling of the adsorption behaviour of Sod-ZMOF/Chitosan Material during CO_2 capture: A preliminary study

7.1 Introduction

This study was carried out as an extended part of this research. A preliminary investigation was carried out to test the adapted models in this study on sod-ZMOF/chitosan which a composite material with very similar properties to polyaspartamide. The outcome of this study provided a good basis upon which polyaspartamide was studied.

Sodalite-zeolite metal organic frameworks impregnated with chitosan (Sod-ZMOF/Chitosan) are promising composite materials that could be used as adsorbents for CO_2 capture. Various CO_2 capture technologies have also been reported in literature (Zhang et al., 2009: Lueng et al., 2014). Littel et al. (1991), Chiesa and Consonni (1999) reported physical absorption of CO_2. Bishnoi and Rochelle (2000) worked extensively on Chemical absorption of CO_2, Harlick and Tezel (2004) as well as Cheng and Tan (2009) presented CO_2 capture using the adsorption technology while Powelle and Qiao (2006) presented CO_2 capture using the membrane technology. They all concluded that all these technologies have their disadvantages during CO_2 capture from power plants because of the existence of a significant mass transfer limitation in the process and the high amount of flue gas needed to be pre-treated.

The preferential adsorption of CO_2 onto porous membranes and adsorbents is the basis for CO_2 capture by adsorption (Lueng et al., 2014). Finding a very suitable adsorbent or membrane material that will sufficiently capture CO_2 is the first and most important step in every CO_2 capture process (Dantas et al., 2011).

New classes of porous materials called Sodalite-Metal Organic Frameworks (Sod-MOFs) impregnated with Chitosan for adsorption process was developed. It is envisaged to exhibit an excellent performance in capturing carbon dioxide from a flue gas mixture but its behaviour during CO_2 capture is not widely reported. Experiments have been conducted and reported in literature on the application of Sod-ZMOFs for post-combustion CO_2 capture (Sabouni, 2013). However, reports on the modelling of the adsorption behaviour of Sod-ZMOF/Chitosan during CO_2 capture are still limited. Understanding the behaviour and

performance of this adsorbent, especially when impregnated with chitosan, during post combustion CO_2 capture is very essential. On this note, modelling will be a very useful tool to understand the behaviour of the adsorbent during the CO_2 capture process.

This chapter is devoted to investigating the adsorption behaviour of Sod-ZMOFs/chitosan material which is a MOF of the Sodalite topology with chitosan impregnation for post combustion CO_2 capture via mathematical modelling and simulations. The adsorption technology was considered in this study because of its system simplicity and its very promising low energy consumption (Zhang et al., 2009). In addition, the adsorbent considered in this study is Sodalite-Zeolite Metal Organic frameworks grafted with Chitosan (Sod-ZMOFs/Chitosan) because of its good physical properties such as porosity, high thermal stability, fast adsorption kinetics etc. which is similar to that of polyaspartamide. The CO_2 adsorption capacity of Sod-ZMOFs/Chitosan was determined experimentally and compared with that obtained from the mathematical models in this study. In addition, this study also gives further insight into the effects of temperature on the adsorption capacity of Sod-MOFs/Chitosan during CO_2 capture.

Chitosan-impregnated Sod-ZMOF material have displayed similar characteristics with polyaspartamide as both have the same thermal stability, porosity, rich amine content and are both polymer-based adsorbents. The study contained in this chapter was used as a preliminary investigation to the actual adsorption experiment with polyaspartamide in order to test the selected models whether they are fit to describe a gas-solid adsorption process using polymer-based materials, identify key concepts relating to gas-solid adsorption processes, refine the research questions so that it falls within the limits of the main study and to get an idea about the most suitable method to be adapted by seeing how similar experiments have been done before.

7.2 Metal Organic Frameworks (MOFs)

In recent times, metal organic frameworks have attracted a considerably high attention as a potential adsorbent for CO_2 capture. This is attributed to its large surface area, tuneable pore surface property which makes tuning so easy by either changing the metallic clusters or the organic ligands (Yu et al., 2012). MOFs represent a class of porous materials that offer a lot of advantages in the area of CO_2 capture. In addition to the aforementioned properties MOFs have a high thermal and mechanical stability as well as a well characterized porous and

crystalline structure. The excellent thermal and mechanical stability, better inter-atomic gas interaction, high porosity and free pore volume as well as high flexibility of MOFs make it outstanding and more suitable over conventional zeolite materials. CO_2 capture onto metal organic frameworks at room temperature was reported by Milward and Yaghi (2005) . As a result of the findings by Milward and Yaghi (2005), new and modified types of metal organic frameworks (MOFs) for CO_2 capture were developed by Banerjee et al (2008). Furthermore, MOFs have also proven to be a potential adsorbent for CO_2 capture because it has exhibited an exceptionally high CO_2 adsorption capacity during CO_2 capture with 100% CO_2 at high pressures (Yu et al., 2012). However, the adsorption capacity got drastically reduced when exposed to a flue gas mixture. In order to improve the adsorption capacity of MOFs for CO_2 capture from a mixture of flue gas, this study seeks to impregnate chitosan material onto metal organic frameworks. The CO_2 adsorption capacity remarkably improved when Sod-ZMOFs/chitosan was used as an adsorbent in this study which could be attributed to the good adsorption properties of Chitosan which is very rich in amine.



Fig. 7.1 Metal organic frameworks

7.3 ZMOFs as an adsorbent for CO_2 Capture

Carbon-based materials for physical adsorption such as zeolites are often regarded as benchmark materials for CO_2 capture. Based on its well-defined pore shape and narrow pore size distribution, the application of zeolite is being widely used industrially. Zeolites have displayed very promising results in separating carbon dioxide (CO_2) from a flue gas stream (Creamer and Gao, 2016). Zeolite-like metal organic frameworks (ZMOFs) which are a sub-class of the conventional metal organic frameworks (MOFs) tend to differ from other types of MOFs because they have a negatively charged framework. ZMOFs are considered as promising and appropriate adsorbent for gas adsorption because of the charge compensating extra framework cations in ZMOFs which helps in maintaining its charge neutrality (Breault and Huckaby, 2013). ZMOFs can either be of the Sodalite or rhombic topology.

7.4 Adsorption of CO_2 onto Sod-ZMOFs/Chitosan Material

Sod-ZMOF is a zeolite-based metal organic framework of the sodalite topology. It was first synthesized for gas adsorption by Lui et al in 2006. The anionic framework of Sod-ZMOFs and the extra framework cations in the pores helps in improving its molecular interaction and gas separation capability. Cheng et al (2016) investigated the adsorption of CO_2 on Sodalite metal organic frameworks and Zeolite imidazolate framework (ZIF) which is analogous in structure with Sod-ZMOF. Cheng et al (2011) in their study inferred that Sod-ZMOF displays a higher adsorption capacity for CO_2 than ZIF. This is as a result of the compensating extra framework ions contained in the cavities of Sod-ZMOFs. In addition to the merits of sod-ZMOFs, it has also displayed a high thermal stability to as high as 250℃ and it also displays an appreciably high affinity for CO_2 molecules because of the positively charged ions (cations) inside the pores of sod-ZMOFs. Despite the merits of Sod-ZMOF, this study seeks to investigate Sod-ZMOF/Chitosan (with chitosan impregnation) because it is envisaged that since chitosan is very rich in amine, it will improve the adsorption capacity of the ordinary Sod-ZMOF.

Furthermore, the chitosan material impregnated into Sod-ZMOF in this study is a naturally-occurring material directly derived from chitin. Studies have also shown that after cellulose, chitosan is the most bountiful natural occurring polysaccharide in the universe (Sun et al., 2011). Its derivation is also very simple as it could be derived directly from natural-occurring sources such as the exoskeleton of insects, crustacean shells, shrimps, crabs, and beaks of cephalopods, prawns as well as the cell walls of fungi.

Chitosan is a biomaterial that is renewable, biocompatible, biodegradable, non-antigenic and non-toxic hence it is called a '*green material'*. Chitosan-based nanomaterials are envisaged to be very suitable for CO_2 capture because of their superiority in terms of their physical properties which includes porosity of the material, high surface area and their increased mechanical properties.

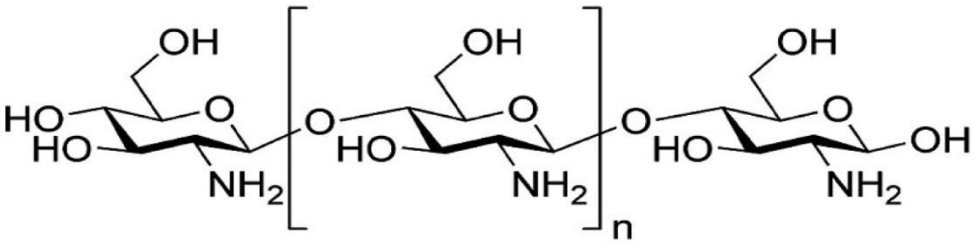


Figure 7.2. Structure of Chitosan (Chen et al., 2011)

More so, the presence of the amino and hydroxyl functional groups in chitosan as seen in Figure 7.2 increases its potential for CO_2 capture because amine has a strong affinity for CO_2. In addition, other polymers and biological molecules can effectively interact with chitosan-based materials because of the presence of the $–NH_2$ and –OH functional groups in the molecules of chitosan (Borah et al., 2011). Therefore, impregnation of chitosan on ZMOFs is expected to improve its adsorption capacity. On this note, the CO_2 adsorption capacity of Sod-ZMOFs/Chitosan is expected to be higher than that of ordinary Sod-ZMOFs. This study is devoted to investigating the CO_2 adsorption behaviour of Sod-ZMOF with chitosan impregnated in it via mathematical modelling so as to be furnished with a deep understanding of the behaviour of this composite material during CO_2 capture.

7.5 Experimental

The adsorbent used in this study was Sod-ZMOFs/Chitosan and it was synthesized from modified protocol described elsewhere (Chen et al., 2011). Sod-ZMOF was synthesized using the method adapted from the work reported in literature (Ai et al., 2011). For preparation of chitosan, chitin was sieved and subjected to demineralization, de-proteinization and decolonization. Chitin used in this work was produced from exoskeletons of crabs. The procedure used for impregnation of chitosan was adapted from the work reported in literature (Sun et al., 2015). Chitosan was first added to acetic acid and stirred under heat for about 1 h after which sod-ZMOF was added under continuous stirring for 1 hour. The resultant suspension was filtered, washed with distilled water to a neutral P^H and dried in an oven at 50℃ for 24 h.

The gases used in this experimental study is a standard mixture of CO_2/N_2 (15 % CO_2 v/v 85% N_2) supplied by Afrox (Pty) South Africa. The Sod-ZMOF/chitosan adsorbent was pre-treated in the adsorption column by passing in Nitrogen gas through the packed bed adsorption column at a flowrate of 1.5 ml/s and a temperature of 100℃ for about one hour to

remove impurities. The temperature of the adsorption bed was adjusted to 60, 45, and 30 ^{o}C after the pre-treatment stage under N_2 flow. The flue gas mixture (15 % CO_2/85% N_2 v/v) was then fed into the adsorption bed at a flow rate 2.5 ml/s and the adsorption column was by-passed in order to first determine the initial concentration of CO_2 from the ABB-AO2020 gas analyser. The gas flow rate was regulated using a mass flow controller and the outlet CO_2 concentrations were obtained from the ABB-AO2020 gas analyser. The experiments reported in this study were conducted at isothermal conditions. The models used to describe the behaviour of Sod-ZMOF/Chitosan have been discussed in the model description section in Chapter 3 of this dissertation.

7.6 Results and Discussion

Figure 7.3 shows a breakthrough curve for the adsorption of CO_2 on Sod-ZMOF/chitosan at 30, 45 and 60 ^{o}C. Figure 7.4 shows a breakthrough curve at 30^{o}C fitted to the Bohart-Adams model. In Figure 7.4, the Bohart-Adams model did not describe the initial part of the breakthrough curve but it clearly described the latter part of the breakthrough curve. This simply means that the model alone cannot sufficiently describe the behaviour of Sod-ZMOF/Chitosan; hence kinetic models were also studied. Table 7.2 presents the model parameters obtained from the solutions in MATLAB R2014a. Bohart-Adams model also predicted a higher amount of CO_2 adsorbed by the material which is closer to that obtained experimentally. A maximum of 1.9 mmol of CO_2 per gramme adsorbent was obtained as the amount of CO_2 adsorbed by the adsorbent from the experiment while the 1st order kinetic model predicted that a maximum of 1.8 mmol CO_2 per gramme of adsorbent was adsorbed by the material and the Pseudo 2nd order predicted a maximum of 1.7 mmol of CO_2 per gramme of adsorbent. From the breakthrough curves in Figures 7.3 and 7.4 as well as the adsorption curve in Figure 7.5 , it could be inferred that the adsorption of CO_2 on Sod-ZMOF/Chitosan showed a two-stage adsorption process under the specified conditions with a rapid initial uptake of CO_2 and subsequently a slow adsorption process. This two-stage adsorption process observed in this study is similar to that observed during the adsorption of CO_2 on calcium oxide (Xiong et al., 2003) , Lithium Zirconate (Bhatia and Pelmutter,1983) and porous magnesium oxide (Song et al., 2016). The two-stage adsorption observed in this study could be attributed to the adsorption products generated on the surface of the adsorbent and the porosity distribution within the material. The adsorption products generated on the surface of the adsorbent slowed down the diffusion of CO_2 into the inner part of the particle thereby

lowering the rate of adsorption of CO_2 on this adsorbent. The plots at different temperatures all showed a non-linear relationship. The Bohart-Adams model perfectly describes the latter part of the breakthrough curve at 30^{o}C, but does not describe sufficiently the initial part of the curve because a rectangular or step isotherm as well as gradients in axial direction was assumed for the model and these assumptions did not completely favor the adsorbent under investigation in this study. In Table 4.1, the adsorption temperature showed a distinct effect on the adsorption behaviour of Sod-ZMOF/chitosan. A higher concentration of CO_2 was adsorbed at very low temperatures. This is perfectly in agreement with literature reports that lower temperatures favour the adsorption process. From the breakthrough curve in Figure 7.3, 80% vol/vol of CO_2 was adsorbed by the adsorbent and equilibrium was attained after 900 seconds at 30^{o}C. At 45^{o}C, 70% v/v CO_2 was adsorbed and equilibrium was attained after 750 seconds while at a maximum temperature of 60^{o}C, a minimum of 55% vol/vol CO_2 was adsorbed on the surface of Sod-ZMOF/Chitosan, equilibrium faster at 700 seconds. This clearly explains that the kinetics of adsorption of CO_2 onto sod-ZMOF/Chitosan is not too fast therefore it could be studied using kinetic models. From the adsorption curves reported in this study, it can be speculated that adsorption started rapidly at the initial stage after 50 seconds while the slow adsorption stage lasted for about 1000 seconds. This is due to the inter-particle diffusion resistance which could be attributed to the pore size distribution of the adsorbent. Film diffusion resistance controlled the adsorption of CO_2 on the sod-ZMOF/chitosan material at the initial stage but upon diffusion of the CO_2 on the gas film, intra-particle diffusion became a rate-limiting step in the adsorption process until adsorption equilibrium.

From the normalized standard deviation of the kinetic models in Table 7.1, it is clearly seen that the Lagergren's pseudo-first order model predicted the amount of CO_2 adsorbed with a smaller error than the Lagergren's pseudo-second order model. The pseudo 1st order model had a minimum and maximum percentage error of 3.72 % and 5.6 % respectively. While the pseudo 2nd order model predicted the maximum amount of CO_2 adsorbed on Sod-ZMOF/Chitosan with a maximum percentage error of 8.32 % and a minimum error of 7.44 %. These errors could be attributed to some minor experimental errors in the course of the experiment. The Lagergren's pseudo-first order model was also more consistent with the experimental results as seen in Fig 6. The pseudo-first order model best described the adsorption of CO_2 unto Sod-ZMOF/Chitosan material. As reported by Gupta and Bhattacharya (2011), the pseudo-1st order model is well suited in describing the adsorption

process on physical adsorbents while the pseudo-second order is best suited to describe a process involving chemical adsorption (Song et al, 2016). On this note, it can be speculated that physical adsorption governs the adsorption of CO_2 onto the Sod-ZMOF/Chitosan material in this study. However, estimation of the adsorption enthalpies will be necessary to make a logical conclusion.

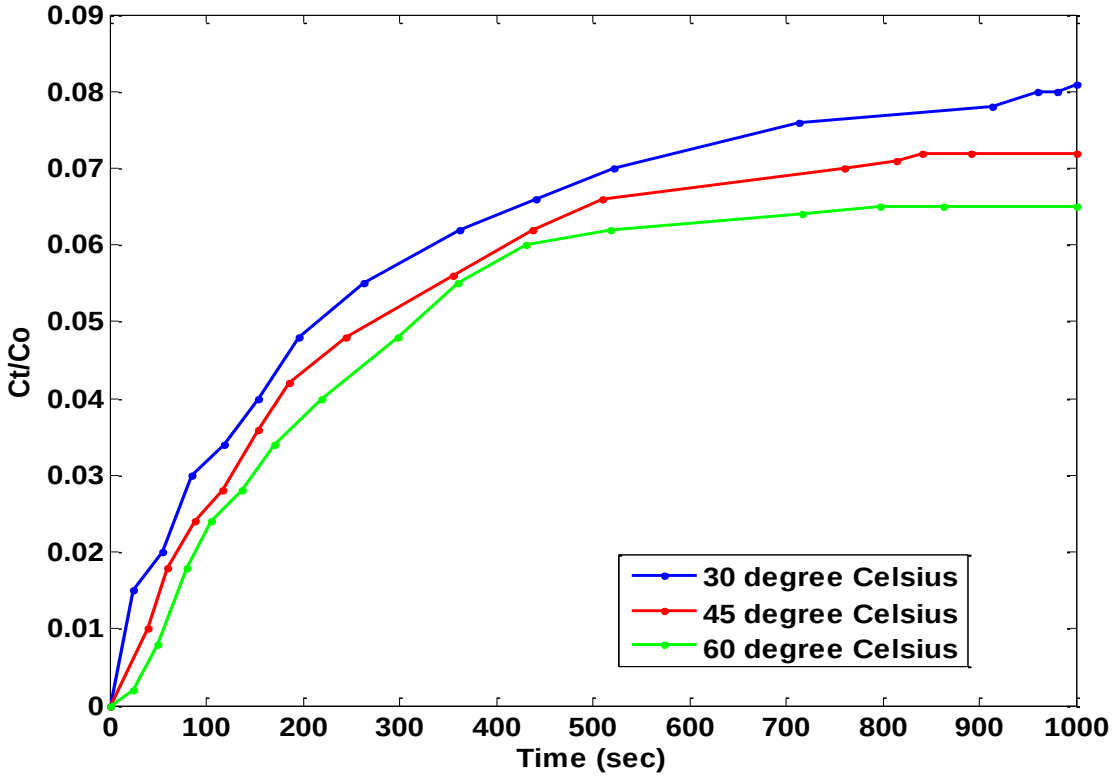


Figure 7.3 Experimental Breakthrough curves of 15 % CO_2 balance N_2 on Sod-ZMOF/Chitosan at various temperatures

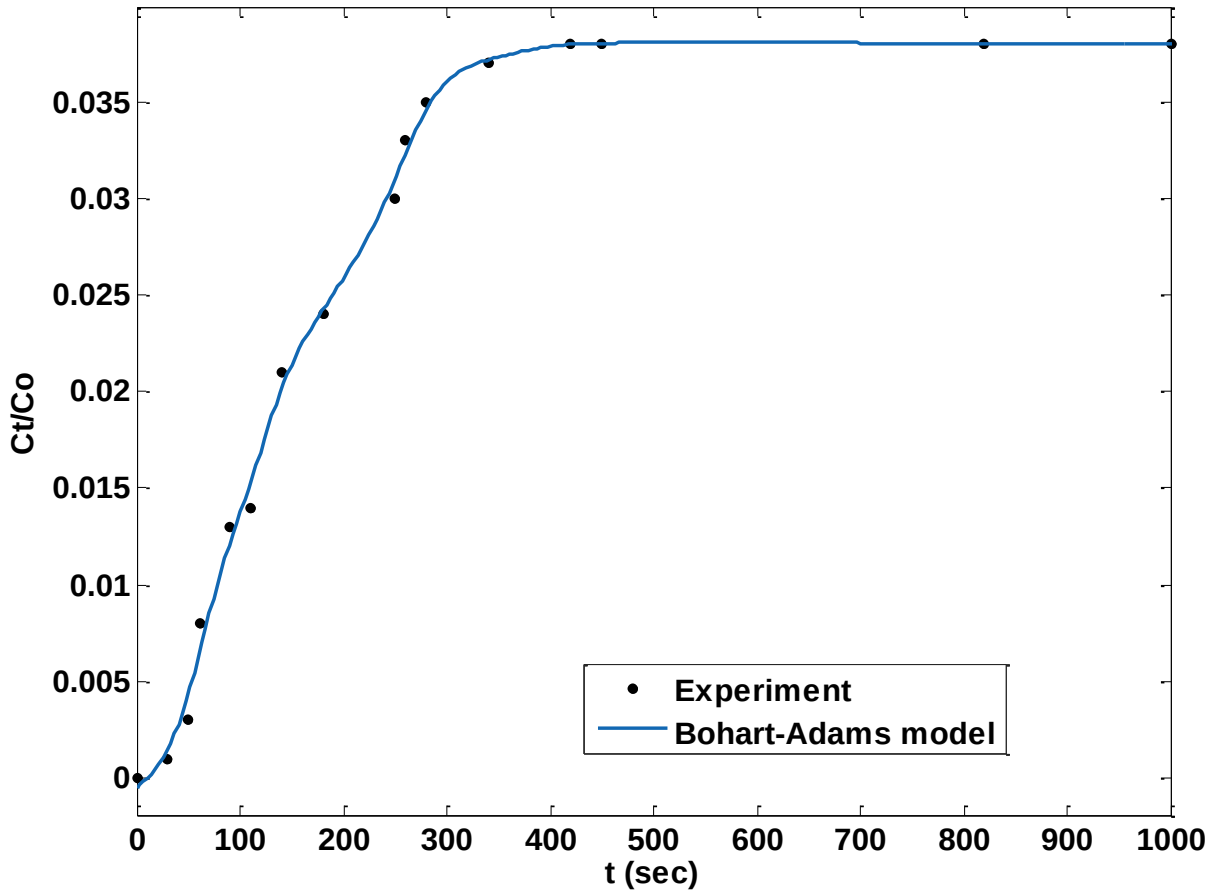
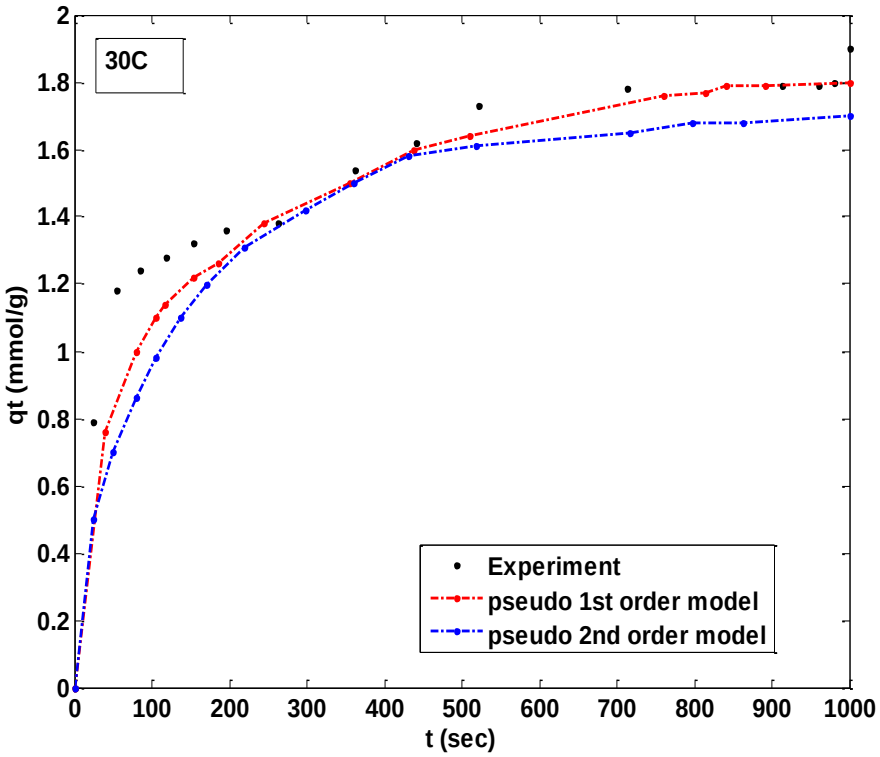
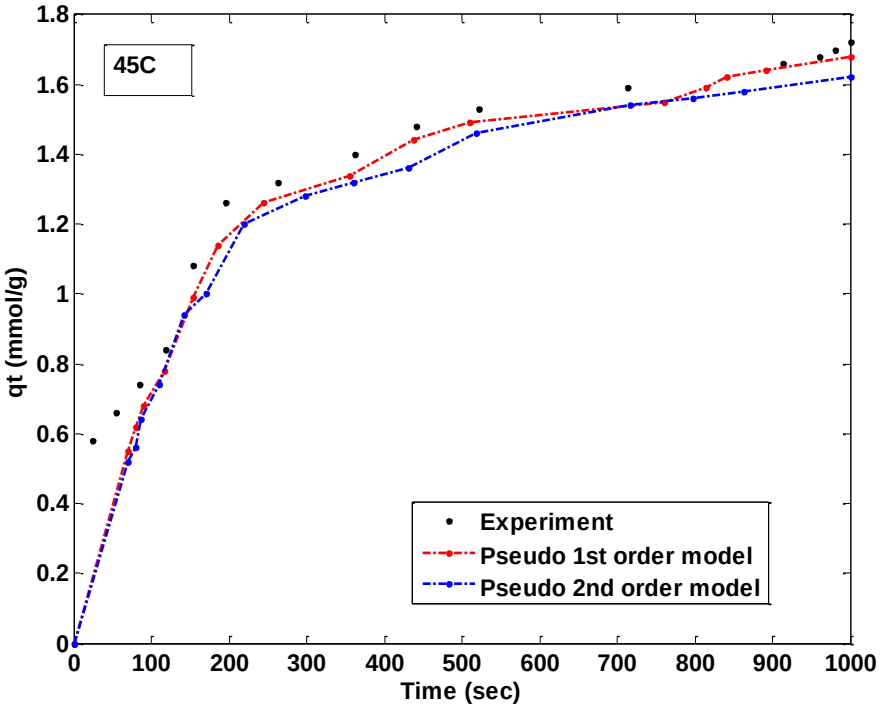


Figure 7.4. Experimental breakthrough curve at 30^{o}C and corresponding fit to the Bohart-Adams model


30C
qt (mmol/g)
t (sec)
Experiment
pseudo 1st order model
pseudo 2nd order model
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
0
100
200
300
400
500
600
700
800
900
1000


45C
qt (mmol/g)
Time (sec)
Experiment
Pseudo 1st order model
Pseudo 2nd order model
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
0
100
200
300
400
500
600
700
800
900
1000

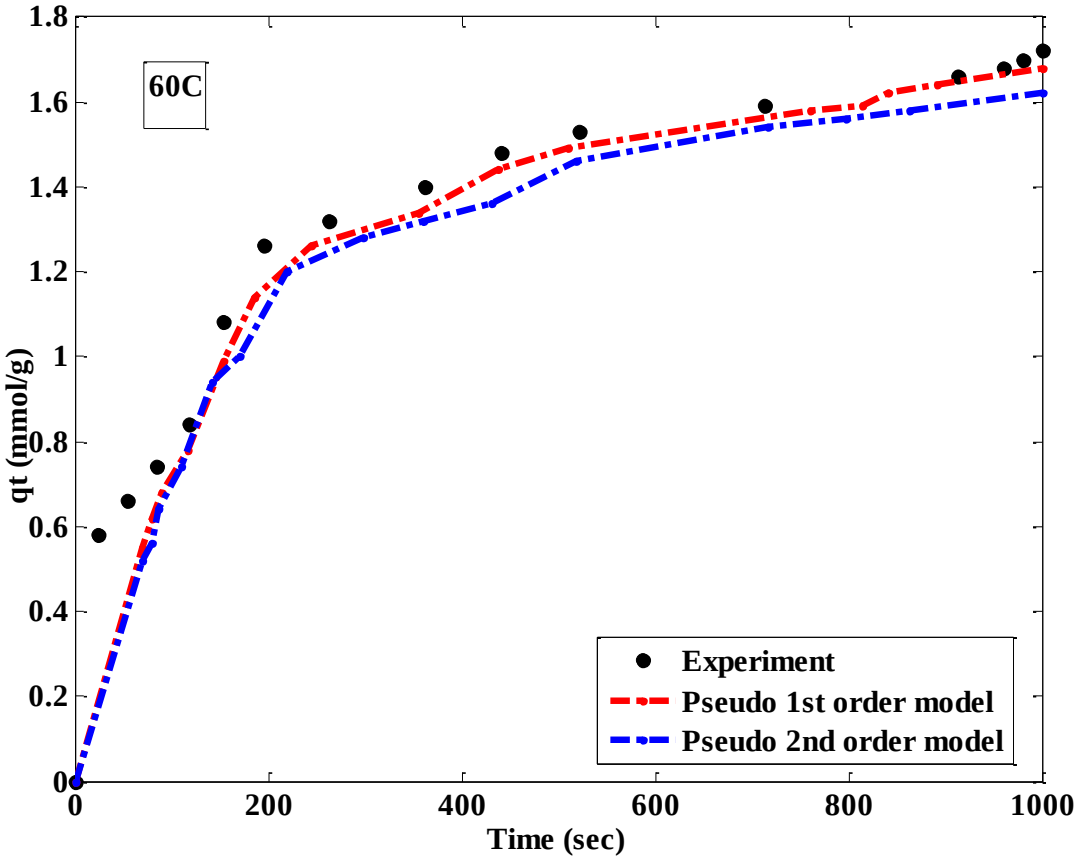


Figure 7.5. Experimental and predicted CO_2 adsorption curves of Sod-ZMOF/Chitosan material at constant pressure and different temperatures; (A) 2bar, 30^{o}C, (B) 2bar 45^{o}C (C) 2bar 60^{o}C

Table 7.1 Kinetic parameters of pseudo 1st and 2nd order models under different adsorption conditions

		Pseudo 1st order			Pseudo 2nd order	
Adsorption Condition	q_{exp}	q_{cal}	Δq Error (%)	q_{exp}	q_{cal}	Δq Error (%)
2bar, 30C	1.9	1.8	3.72	1.9	1.7	7.44
2bar, 45C	1.7	1.58	4.99	1.7	1.5	8.32
2bar, 60C	1.39	1.28	5.60	1.39	1.24	7.63

Table 7.2 Mathematical relations and corresponding model parameters

Models Studied	Model Parameters				Mathematical Equation
Bohart-Adams	*Kb*		*q*		$\ln(C/Co) = K(Cot - q.\frac{z}{v})$
	0.184		1.8		
Pseudo 1st order		K_f			$q_t = q_e(1 - e^{-Kft})$
		30°C	45°C	60°C	
		0.07	0.075	0.08	
Pseudo 2nd order		K_s			$q_t = \frac{q_e^2 K_s t}{1 + q_e K_s t}$
		0.076	0.078	0.079	

7.7 Summary

The CO_2 adsorption behaviour of Sod-ZMOF/Chitosan was studied under various adsorption temperatures and at a constant pressure and flowrate of 2 bars and 2.5 ml CO_2/s, respectively. Sod-ZMOF/Chitosan exhibited a two-stage CO_2 adsorption process characterized by a rapid initial step and a sluggish following step. The initial step which was reported to be very fast in this study was as a result of film diffusion from the bulk gas phase to the surface of the sod-ZMOF/Chitosan material. The latter step which was reported to be slow was attributed to intra-particle diffusion resistance as a result of the narrow pores on the adsorbent which hampers on the CO_2 diffusion rate. This study also revealed that the sluggish diffusion of CO_2 onto Sod-ZMOF/Chitosan had effect on the adsorption kinetics of the Sod-ZMOF/Chitosan material. The Lagergren's pseudo-first and second order models were used to fit the experimental adsorption curves of Sod-ZMOF/Chitosan. The accuracy of the predictions by these kinetic models were tested using an error function based on the normalized standard deviation as presented in literature by Song et al (2016). The Lagergren's pseudo-first perfectly described the kinetics of adsorption of CO_2 onto Sod-ZMOF/Chitosan at various temperatures in this study. The least error was also reported by the Lagergren's-first order kinetic model. Based on this, it can be concluded that the mechanism of adsorption of CO_2 onto Sod-ZMOF is governed by physisorption. Sod-ZMOF/Chitosan also displayed good adsorption characteristics under various temperatures, it had a relatively fast kinetics therefore it is speculated that Sod-ZMOF/Chitosan is a promising adsorbent for post-combustion CO_2 capture based on its general behaviour in this study.

Finally, this study also confirms reports from literature that high pressure and low temperature favours adsorption process because the highest amount of CO_2 adsorbed by the adsorbent in this study was obtained at a high pressure of 200 kPa and at the lowest temperature of 30 ^oC while at a higher temperature of 60 ^oC in this study, a lower amount of CO_2 was adsorbed. On this note the mathematical models explored as well as other mathematical models were also applied to study the behaviour of polyaspartamide.

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CHAPTER EIGHT

General Conclusions and Recommendations

This chapter summarizes the main findings of this study and also provides some recommendations for future research.

8.1 General Conclusions

Undoubtedly, global warming due to the emission of CO_2 into the atmosphere is raising serious concerns globally. CO_2 emission is on the increase because of industrialization and economic growth. CO_2 capture and storage (CCS) is a promising option for reduction of global CO_2 emissions. Absorption of CO_2 using monoethanolamine has been widely embraced and regarded as a matured technology for CO_2 capture. But due to the challenges such as high energy requirement for solvent regeneration and corrosive nature of sorbents, the adsorption technology using solid sorbents is now being considered as an alternative technology for CO_2 capture. Adsorbents play a vital role in the adsorption technology, it is therefore necessary to have a deep understanding of the behaviour of the adsorbents used for CO_2 capture under different operating conditions. Against this background, the work documented in this dissertation focused on investigating the CO_2 adsorption behaviour of a novel amine-rich polymer-based adsorbent (polyaspartamide) during CO_2 capture using experimental study and modelling approach. The investigative study was successfully carried out. The behaviour of polyaspartamide during CO_2 capture was assessed in terms of its adsorption kinetics, breakthrough curves, mechanism of diffusion and rate-limiting steps. CO_2 adsorption breakthrough curves were obtained experimentally at various temperatures in a packed bed adsorption column and verified theoretically using mathematical models. Several operating parameters such as adsorption temperature, feed flow rate, operating pressure were also used in the models to test the parametric effect of operating variables on the behaviour of polyaspartamide. The behaviour of polyaspartamide in the presence of moisture was also reported. The theoretical results predicted by the models were in close agreement with experimental results. The main findings and conclusions made from this study are listed below:

- The adsorption behaviour of polyaspartamide during CO_2 capture was successfully studied in terms of its adsorption kinetics, breakthrough behaviour, diffusion mechanism, rate-limiting steps and its behaviour in the presence of moisture using

experimental study and modelling approach. Polyaspartamide was confirmed as a promising material for CO_2 capture because of its fast adsorption kinetics, longer breakthrough times and high resistance to moisture shown in this study. Just like other amine-rich polymer-based adsorbent, moisture had a negligible effect on the adsorption capacity of polyaspartamide during post combustion CO_2 capture. Therefore, polyaspartamide is a moisture-resistant material which makes it a very good adsorbent for CO_2 capture from power plants.

- The model by Bohart-Adams predicted a maximum adsorption capacity of 365.64 mgCO_2/g adsorbent while the model adapted from the Polanyi equation with vapour pressure as moisture parameter predicted a maximum adsorption capacity of 354.1 mgCO_2/g adsorbent which is also a very high adsorption capacity. This means that moisture had very little effect on the adsorption capacity of polyaspartamide.
- Kinetic behaviour of polyaspartamide was studied at three different temperatures (303, 318 and 333 K) using Lagergren's pseudo 1st order and 2nd order as well as Avrami kinetic models. It was found that the Avrami kinetic model consistently and accurately described the adsorption of CO_2 onto polyaspartamide at all temperatures studied with the least percentage error ranging from 1.55 - 2.38 %. This simply implies that the adsorption of CO_2 onto polyaspartamide is dominated by physi-sorption rather than chemisorption and the adsorption process is reversible via desorption process. The behaviour of polyaspartamide under a wide range of operating pressures and adsorption temperature is also influenced by the choice of a particular kinetic model.
- Thomas model did not sufficiently describe the adsorption of CO_2 onto polyaspartamide because of the existence of external mass transfer and intra particle diffusion during the adsorption of CO_2 onto polyaspartamide. The adsorption process was controlled by interphase mass transfer. However, the model proposed by Bohart and Adam adequately described the adsorption behaviour of polyaspartamide in this study because of the inclusion of external mass transfer and particle diffusion in the model.
- Film diffusion governed the adsorption of CO_2 onto polyaspartamide and intra-particle diffusion was the rate-limiting step controlling the CO_2 adsorption process in this study. This means that the rate controlling the adsorption of CO_2 onto polyaspartamide is the diffusion of CO_2 within the particle of polyaspartamide. The

rate limiting step determined the actual mass transfer of CO_2 molecule during the adsorption of CO_2 onto polyaspartamide.

- Lower flow rates and temperature had an incremental effect on the adsorption capacity of polyaspartamide because lower flowrate increased the residence time of the gas on the adsorbent thereby enhancing mass transfer between the gas molecules and the adsorbent. Since adsorption is an exothermic process; lower temperatures and higher pressures favour the adsorption of CO_2 onto polyaspartamide; this hypothesis was confirmed in this study.
- Polyaspartamide displayed a high CO_2 capture efficiency at all temperatures studied. Maximum CO_2 adsorption capacity was reported at low temperatures. PAA displayed a CO_2 capture efficiency that was as high as 92.67 % at 303 K and 86.67 % at 333 K. This confirms that polyaspartamide (PAA) is an efficient material for CO_2 capture studies.
- And finally, compared to the Sod-ZMOF/Chitosan composite material studied during the preliminary investigation, polyaspartamide displayed a higher CO_2 adsorption capacity and capture efficiency under similar conditions. Therefore, Polyaspartamide is a more promising material for CO_2 capture than Sod-ZMOF/Chitosan.

8.2 Recommendations for Future Study

Based on the findings of this study, the following recommendations were made for future work:

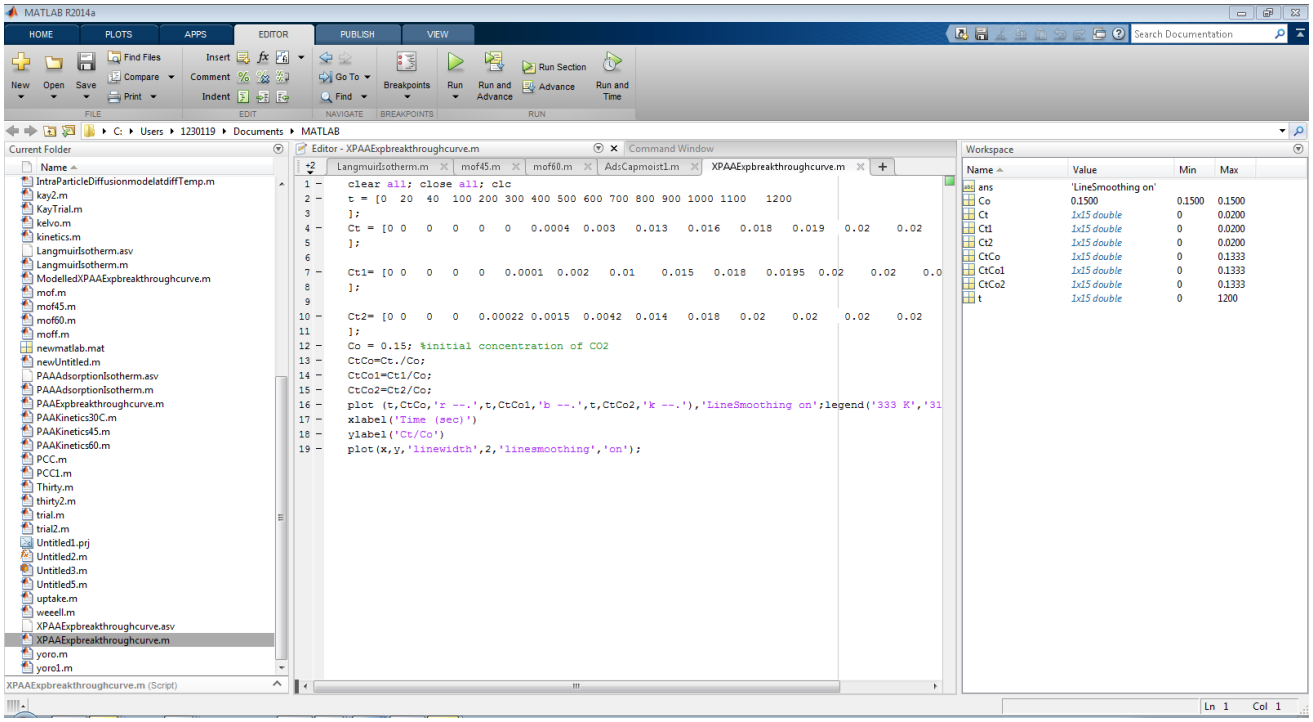
- This study investigated the kinetic behaviour of polyaspartamide during CO_2 capture and important kinetic parameters for process design and optimization were obtained. It is however recommended that a detailed design and optimization of a CO_2 capture system using polyaspartamide as an adsorbent be carried out in the future study.
- Development of gas-solid adsorption models to describe the adsorption of CO_2 onto polymer based adsorbents should also be considered in any future work as this study considered and explored only existing gas-solid adsorption models. Theoretical explanations of the behaviour of adsorbents for CO_2 capture using mathematical models are scarcely reported in literature.
- Quantification of the heat of adsorption is very important for kinetic studies of any adsorption process because the heat released or absorbed during adsorption influences sorbent temperature and thus the rate of adsorption. On this note, the heat of

adsorption of polyaspartamide during CO_2 capture should be studied as well during future kinetic study in order to make a logical conclusion on the kinetic behaviour of the novel material.

- Finally, the issue of scale-up should be explored in order to determine whether polyaspartamide can be synthesized economically which will make it applicable for industrial use. Investigation should also be carried out to understand whether the use of laboratory-scale operating parameters could be realistic if applied at an industrial scale. Optimization studies should be carried out to determine the exact conditions at which adsorption of CO_2 on polyaspartamide will be maximized. An economic evaluation would also be necessary alongside further performance tests to ascertain if the adsorbent can be used on a large scale.

APPENDIX B: MATLAB CODES AND MODEL SOLUTIONS

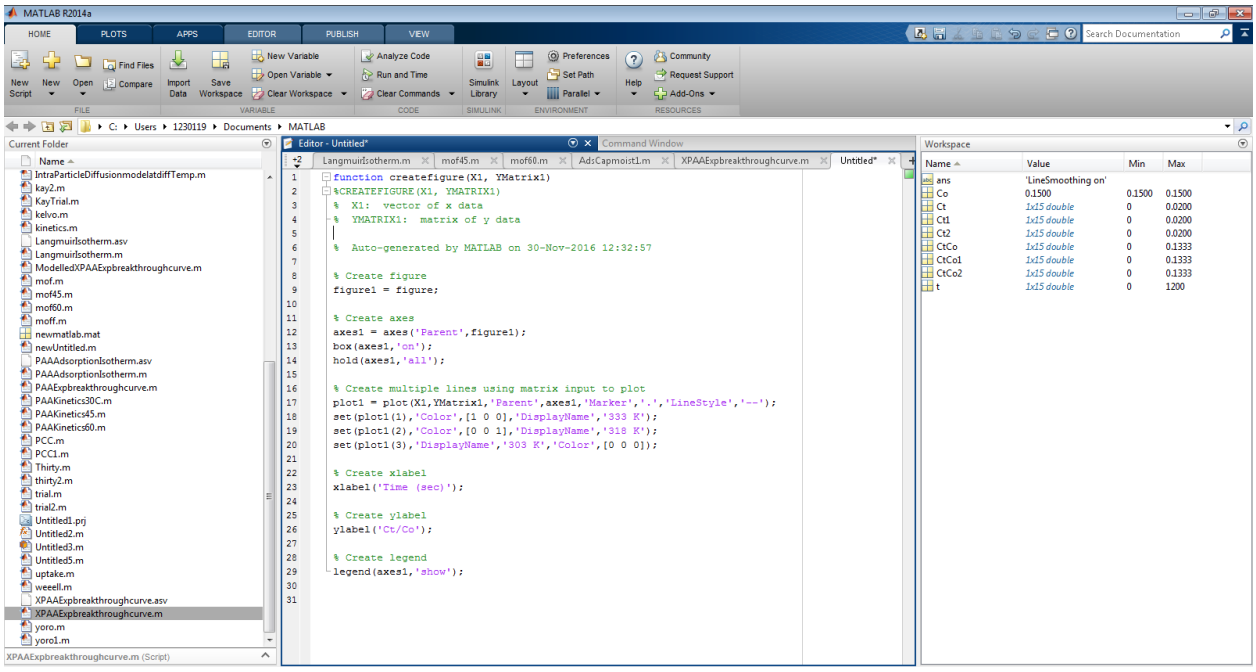
Breakthrough Curves



```
clear all; close all; clc
t = [0  20  40  100 200 300 400 500 600 700 800 900 1000 1100   1200
];
Ct = [0 0   0   0   0   0.0004  0.003   0.013   0.016   0.018   0.019   0.02    0.02
];

Ct1= [0 0   0   0   0   0.0001  0.002   0.01    0.015   0.018   0.0195  0.02    0.02    0.0
];

Ct2= [0 0   0   0   0.00022 0.0015  0.0042  0.014   0.018   0.02    0.02    0.02    0.02
];
Co = 0.15; %initial concentration of CO2
CtCo=Ct./Co;
CtCo1=Ct1/Co;
CtCo2=Ct2/Co;
plot (t,CtCo,'r --.',t,CtCo1,'b --.',t,CtCo2,'k --.'),'LineSmoothing on';legend('333 K','31
xlabel('Time (sec)')
ylabel('Ct/Co')
plot(x,y,'linewidth',2,'linesmoothing','on');
```



```
function createfigure(X1, YMatrix1)
%CREATEFIGURE(X1, YMATRIX1)
%  X1:  vector of x data
%  YMATRIX1:  matrix of y data

%  Auto-generated by MATLAB on 30-Nov-2016 12:32:57

% Create figure
figure1 = figure;

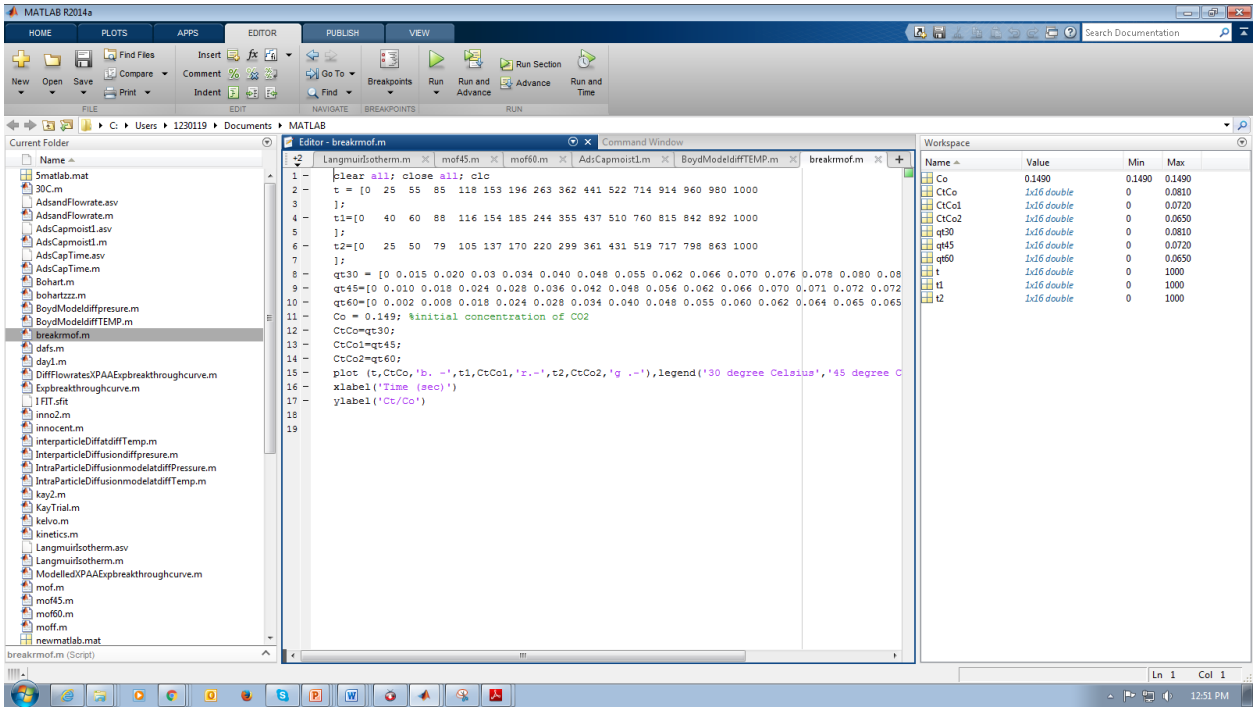
% Create axes
axes1 = axes('Parent',figure1);
box(axes1,'on');
hold(axes1,'all');

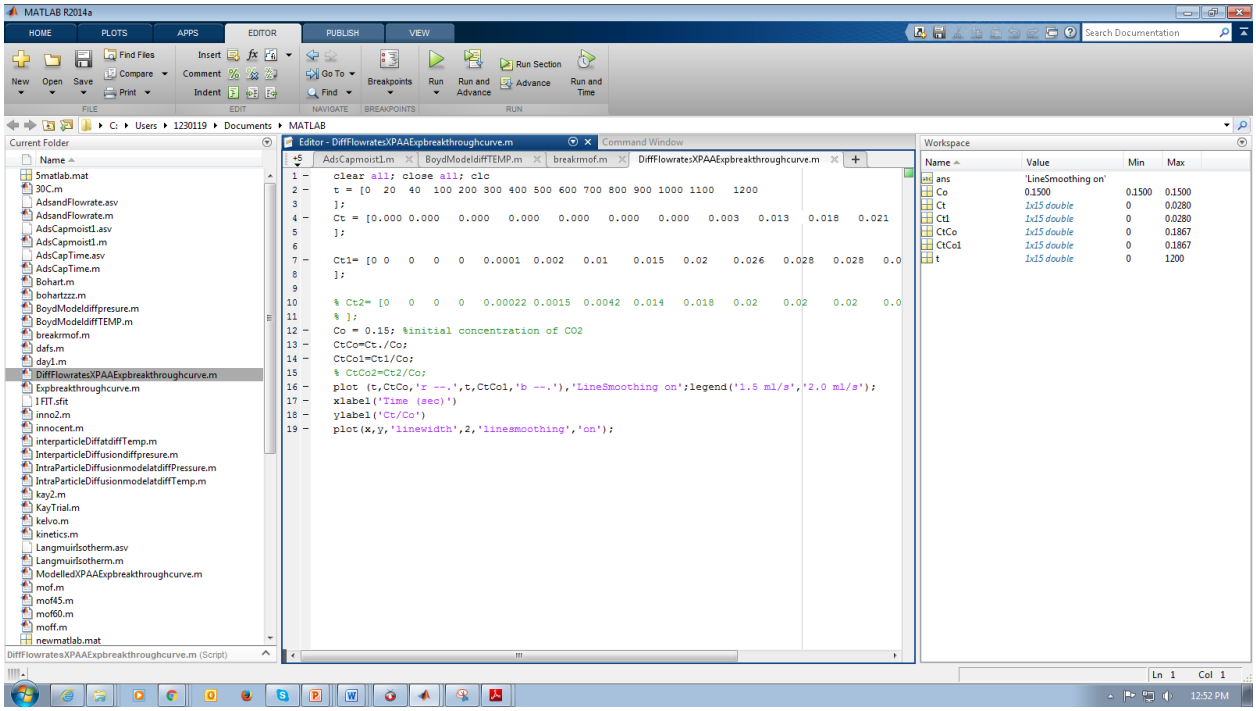
% Create multiple lines using matrix input to plot
plot1 = plot(X1,YMatrix1,'Parent',axes1,'Marker','.','LineStyle','--');
set(plot1(1),'Color',[1 0 0],'DisplayName','333 K');
set(plot1(2),'Color',[0 0 1],'DisplayName','318 K');
set(plot1(3),'DisplayName','303 K','Color',[0 0 0]);

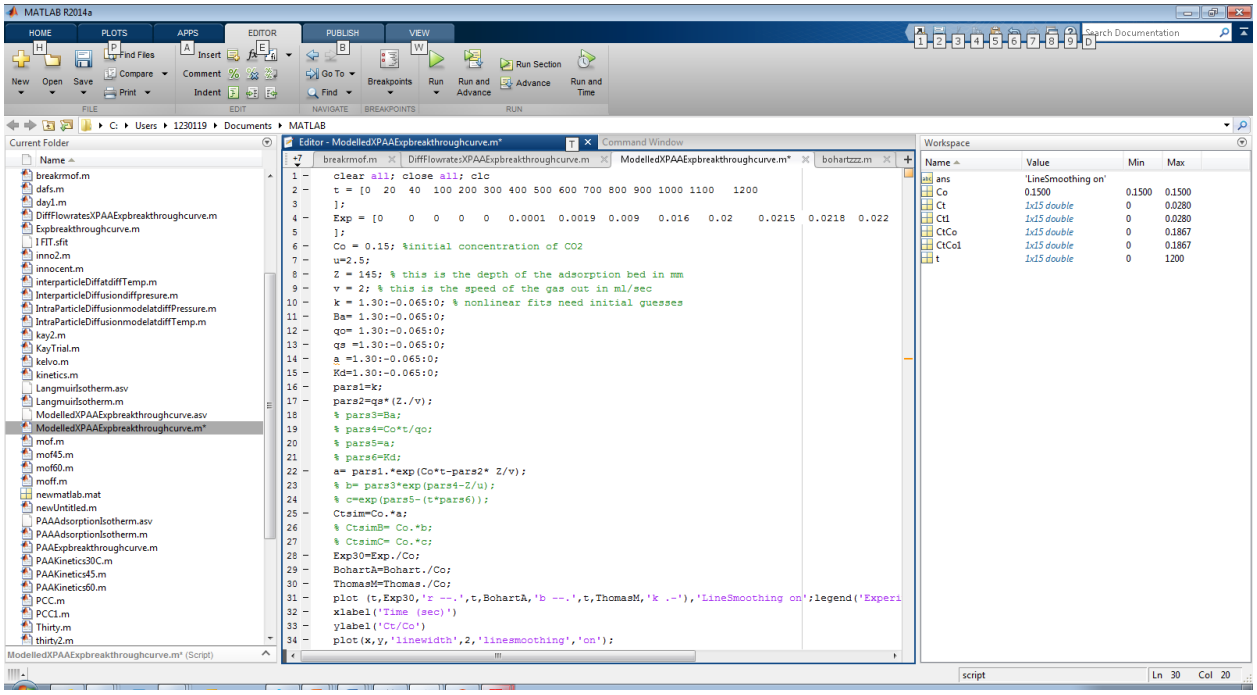
% Create xlabel
xlabel('Time (sec)');

% Create ylabel
ylabel('Ct/Co');

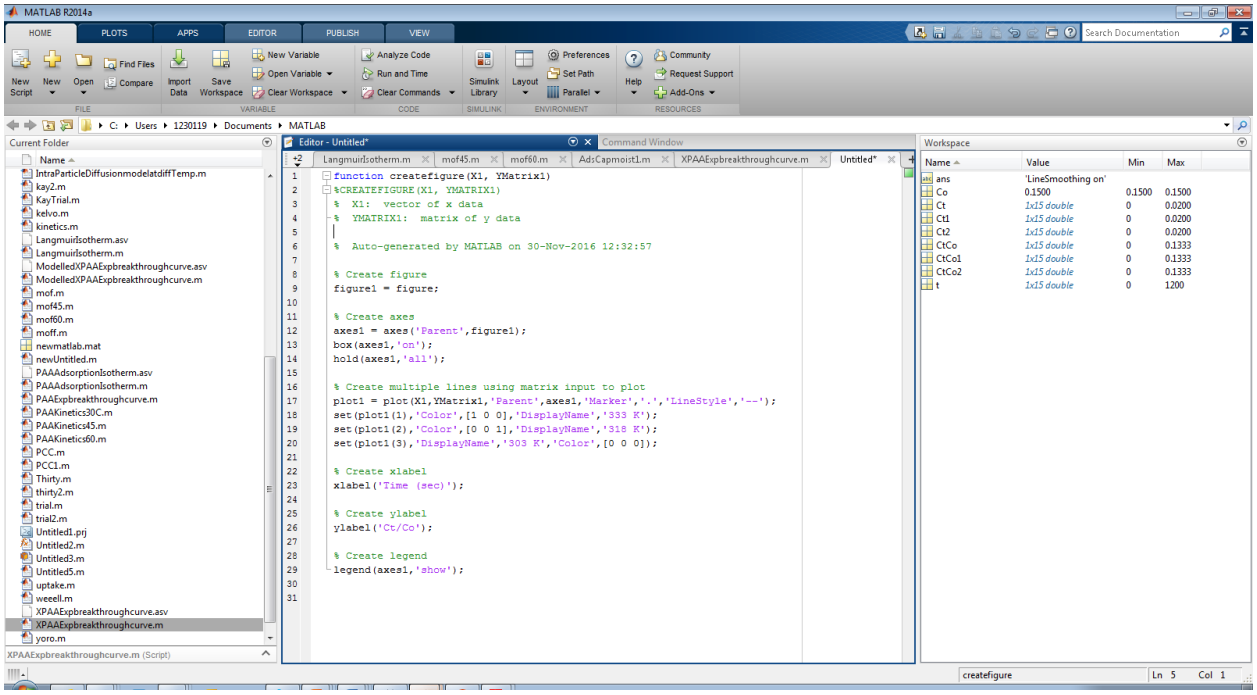
% Create legend
legend(axes1,'show');
```


MATLAB R2014a
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APPS
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Search Documentation
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Save
Find Files
Compare
Print
Insert
Comment
Indent
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Breakpoints
Run
Run and Advance
Run Section
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mof.m
mof45.m
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Editor - breakrmof.m
LangmuirIsotherm.m
mof45.m
mof60.m
AdsCapmoist1.m
BoydModeldiffTEMP.m
breakrmof.m
clear all; close all; clc
t = [0 25 55 85 118 153 196 263 362 441 522 714 914 960 980 1000
];
t1=[0 40 60 88 116 154 185 244 355 437 510 760 815 842 892 1000
];
t2=[0 25 50 79 105 137 170 220 299 361 431 519 717 798 863 1000
];
qt30 = [0 0.015 0.020 0.03 0.034 0.040 0.048 0.055 0.062 0.066 0.070 0.076 0.078 0.080 0.08
qt45=[0 0.010 0.018 0.024 0.028 0.036 0.042 0.048 0.056 0.062 0.066 0.070 0.071 0.072 0.072
qt60=[0 0.002 0.008 0.018 0.024 0.028 0.034 0.040 0.048 0.055 0.060 0.062 0.064 0.065 0.065
Co = 0.149; %initial concentration of CO2
CtCo=qt30;
CtCo1=qt45;
CtCo2=qt60;
plot (t,CtCo,'b. -',t1,CtCo1,'r.-',t2,CtCo2,'g .-'),legend('30 degree Celsius','45 degree C
xlabel('Time (sec)')
ylabel('Ct/Co')
Command Window
Workspace
Name
Value
Min
Max
Co 0.1490 0.1490 0.1490
CtCo 1x16 double 0 0.0810
CtCo1 1x16 double 0 0.0720
CtCo2 1x16 double 0 0.0650
qt30 1x16 double 0 0.0810
qt45 1x16 double 0 0.0720
qt60 1x16 double 0 0.0650
t 1x16 double 0 1000
t1 1x16 double 0 1000
t2 1x16 double 0 1000
Ln 1 Col 1
12:51 PM


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Find
Breakpoints
Run
Run and Advance
Run Section
Advance
Run and Time
C: ▸ Users ▸ 1230119 ▸ Documents ▸ MATLAB
Current Folder
Name
5matlab.mat
30C.m
AdsandFlowrate.asv
AdsandFlowrate.m
AdsCapmoist1.asv
AdsCapmoist1.m
AdsCapTime.asv
AdsCapTime.m
Bohart.m
bohartzzz.m
BoydModeldiffpresure.m
BoydModeldiffTEMP.m
breakrmof.m
dafs.m
day1.m
DiffFlowratesXPAAExpbreakthroughcurve.m
Expbreakthroughcurve.m
FIT.sfit
inno2.m
innocent.m
interparticleDiffatdiffTemp.m
InterparticleDiffusiondiffpresure.m
IntraParticleDiffusionmodelatdiffPressure.m
IntraParticleDiffusionmodelatdiffTemp.m
kay2.m
KayTrial.m
kelvo.m
kinetics.m
Langmuir1sotherm.asv
Langmuir1sotherm.m
ModelledXPAAExpbreakthroughcurve.m
mof.m
mof45.m
mof60.m
moff.m
newmatlab.mat
DiffFlowratesXPAAExpbreakthroughcurve.m (Script)
Editor - DiffFlowratesXPAAExpbreakthroughcurve.m
AdsCapmoist1.m
BoydModeldiffTEMP.m
breakrmof.m
DiffFlowratesXPAAExpbreakthroughcurve.m
clear all; close all; clc
t = [0 20 40 100 200 300 400 500 600 700 800 900 1000 1100 1200
];
Ct = [0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.003 0.013 0.018 0.021
];
Ct1= [0 0 0 0 0 0.0001 0.002 0.01 0.015 0.02 0.026 0.028 0.028 0.0
];
% Ct2= [0 0 0 0 0.00022 0.0015 0.0042 0.014 0.018 0.02 0.02 0.02 0.0
%];
Co = 0.15; %initial concentration of CO2
CtCo=Ct./Co;
CtCo1=Ct1/Co;
% CtCo2=Ct2/Co;
plot (t,CtCo,'r --.',t,CtCo1,'b --.'),'LineSmoothing on';legend('1.5 ml/s','2.0 ml/s');
xlabel('Time (sec)')
ylabel('Ct/Co')
plot(x,y,'linewidth',2,'linesmoothing','on');
Command Window
Workspace
Name
Value
Min
Max
ans 'LineSmoothing on'
Co 0.1500 0.1500 0.1500
Ct 1x15 double 0 0.0280
Ct1 1x15 double 0 0.0280
CtCo 1x15 double 0 0.1867
CtCo1 1x15 double 0 0.1867
t 1x15 double 0 1200
Ln 1 Col 1
12:52 PM



```
clear all; close all; clc
t = [0  20  40  100 200 300 400 500 600 700 800 900 1000 1100   1200
];
Exp = [0    0   0   0   0   0.0001  0.0019  0.009   0.016   0.02    0.0215  0.0218  0.022
];
Co = 0.15; %initial concentration of CO2
u=2.5;
Z = 145; % this is the depth of the adsorption bed in mm
v = 2; % this is the speed of the gas out in ml/sec
k = 1.30:-0.065:0; % nonlinear fits need initial guesses
Ba= 1.30:-0.065:0;
qo= 1.30:-0.065:0;
qs =1.30:-0.065:0;
a =1.30:-0.065:0;
Kd=1.30:-0.065:0;
pars1=k;
pars2=qs*(Z./v);
% pars3=Ba;
% pars4=Co*t/qo;
% pars5=a;
% pars6=Kd;
a= pars1.*exp(Co*t-pars2* Z/v);
% b= pars3*exp(pars4-Z/u);
% c=exp(pars5-(t*pars6));
Ctsim=Co.*a;
% CtsimB= Co.*b;
% CtsimC= Co.*c;
Exp30=Exp./Co;
BohartA=Bohart./Co;
ThomasM=Thomas./Co;
plot (t,Exp30,'r --.',t,BohartA,'b --.',t,ThomasM,'k .-'),'LineSmoothing on';legend('Experi
xlabel('Time (sec)')
ylabel('Ct/Co')
plot(x,y,'linewidth',2,'linesmoothing','on');
```



```
function createfigure(X1, YMatrix1)
%CREATEFIGURE(X1, YMATRIX1)
%  X1:  vector of x data
%  YMATRIX1:  matrix of y data

%  Auto-generated by MATLAB on 30-Nov-2016 12:32:57

% Create figure
figure1 = figure;

% Create axes
axes1 = axes('Parent',figure1);
box(axes1,'on');
hold(axes1,'all');

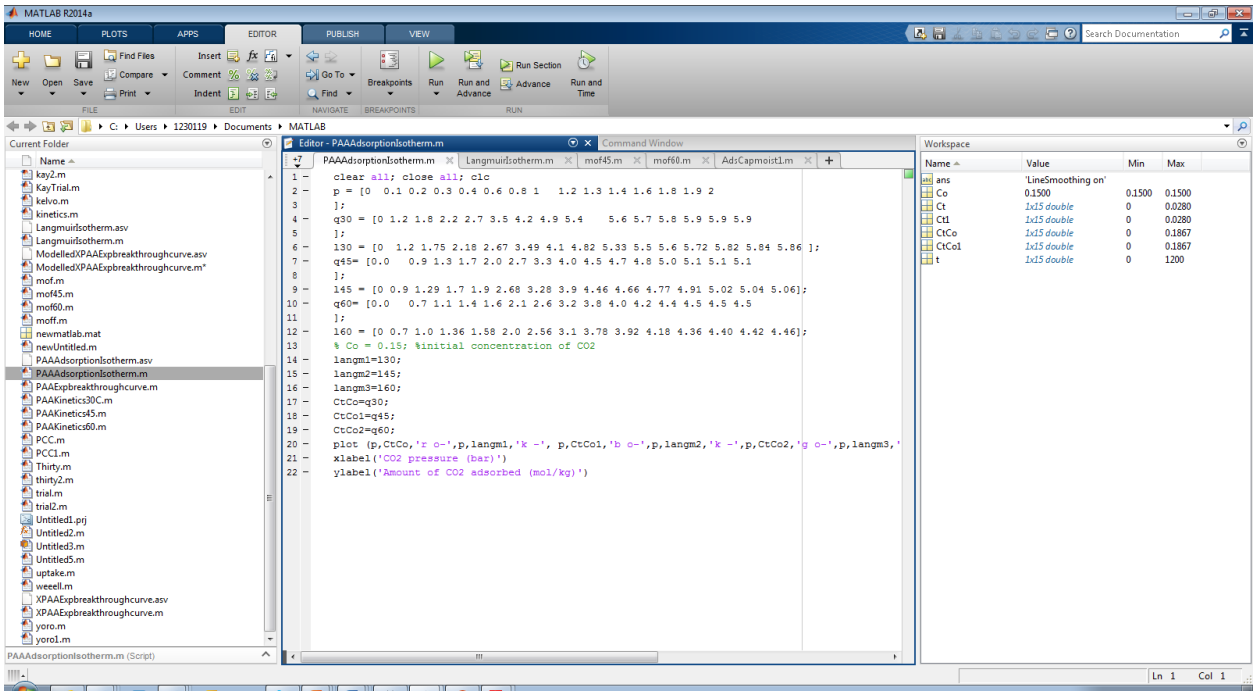
% Create multiple lines using matrix input to plot
plot1 = plot(X1,YMatrix1,'Parent',axes1,'Marker','.','LineStyle','--');
set(plot1(1),'Color',[1 0 0],'DisplayName','333 K');
set(plot1(2),'Color',[0 0 1],'DisplayName','318 K');
set(plot1(3),'DisplayName','303 K','Color',[0 0 0]);

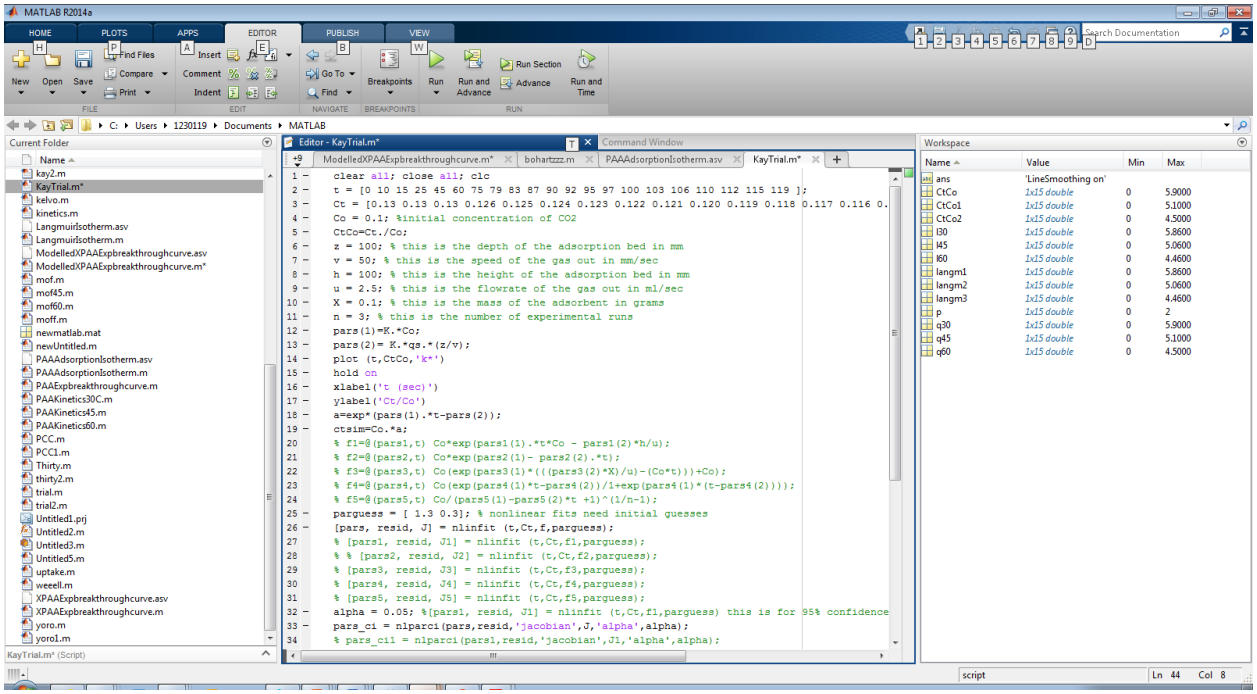
% Create xlabel
xlabel('Time (sec)');

% Create ylabel
ylabel('Ct/Co');

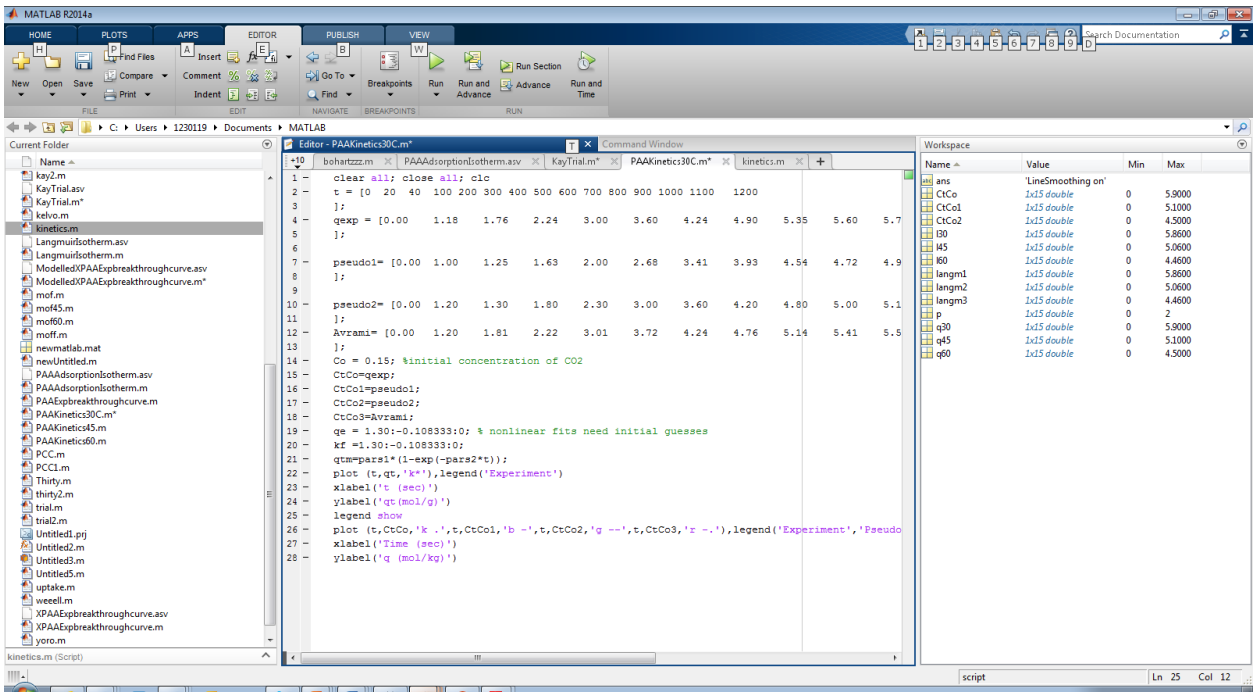
% Create legend
legend(axes1,'show');
```

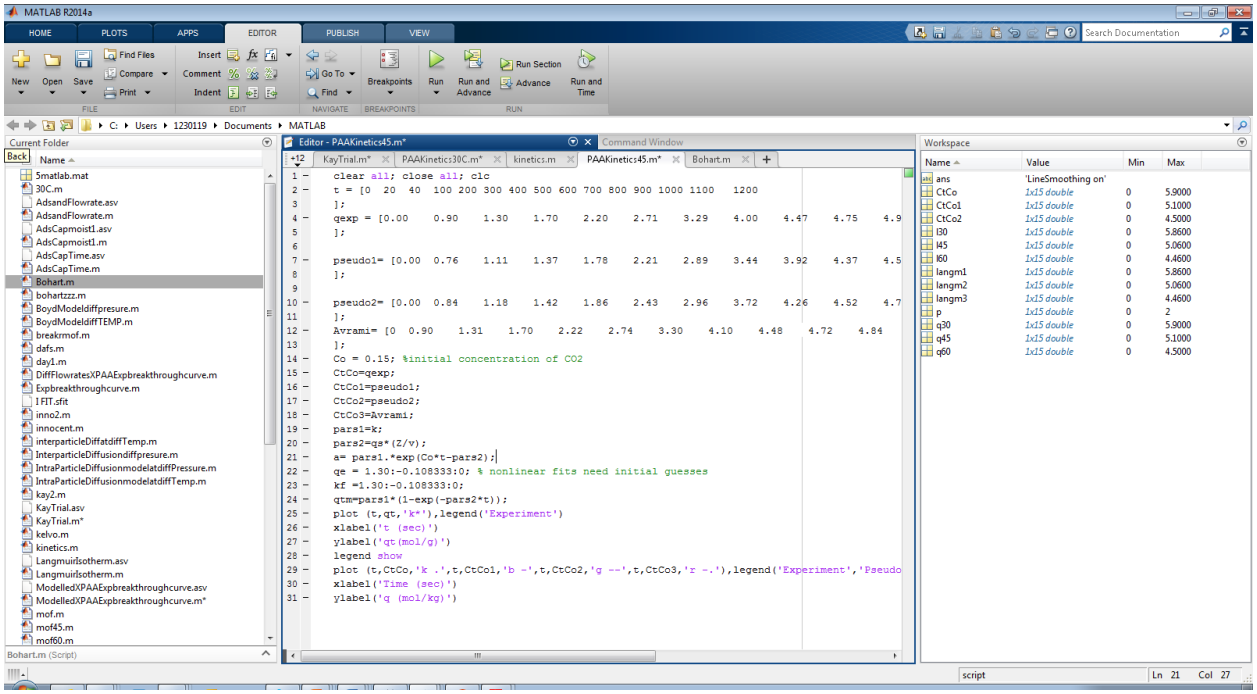
Adsorption Isotherms

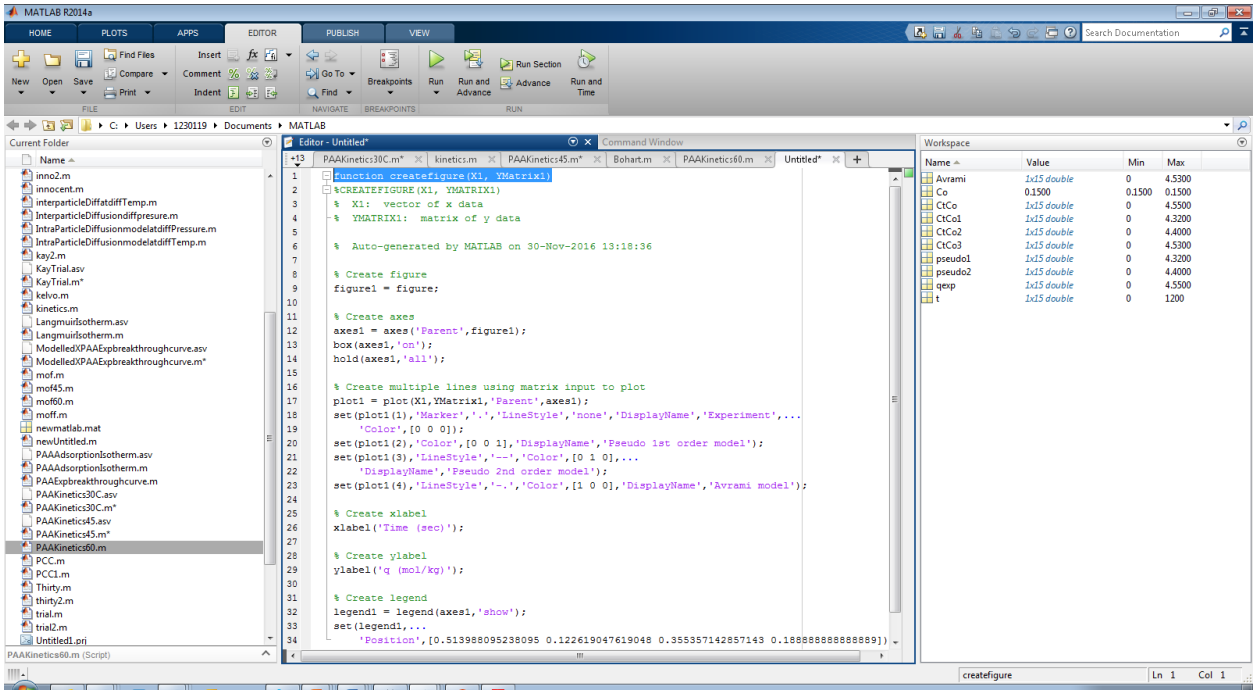




Adsorption Kinetics








```
function createfigure(X1, YMatrix1)
%CREATEFIGURE(X1, YMATRIX1)
%  X1:  vector of x data
%  YMATRIX1:  matrix of y data

%  Auto-generated by MATLAB on 30-Nov-2016 13:18:36

% Create figure
figure1 = figure;

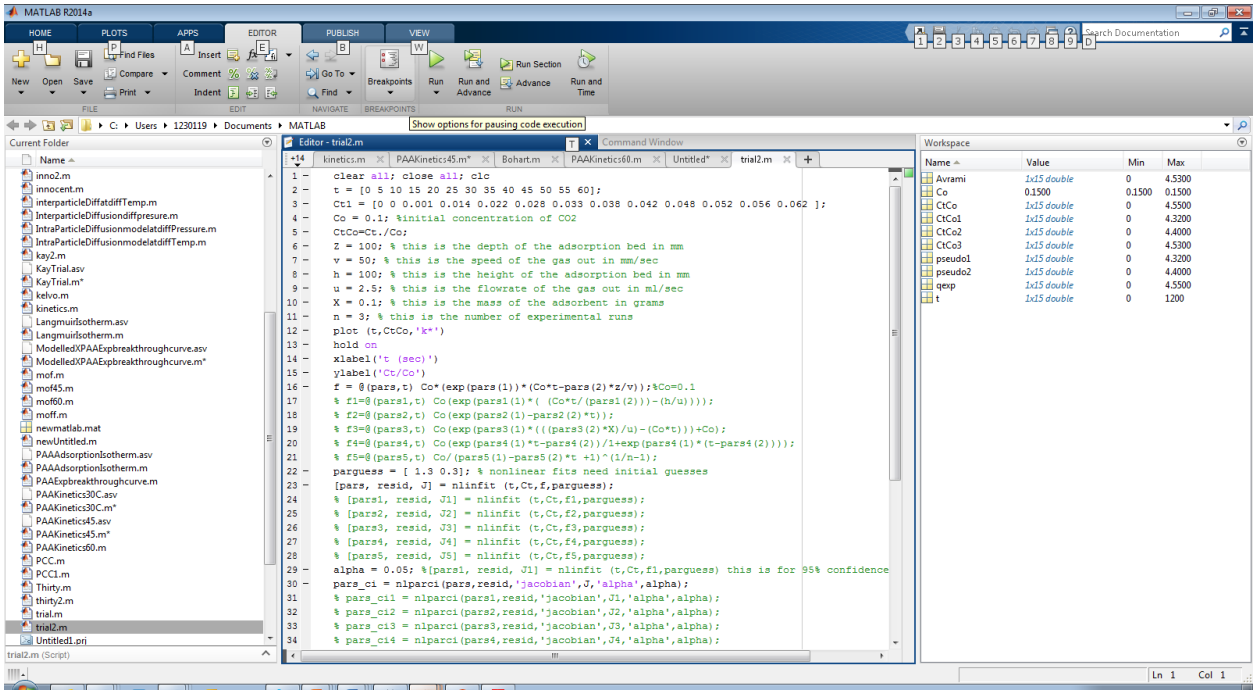
% Create axes
axes1 = axes('Parent',figure1);
box(axes1,'on');
hold(axes1,'all');

% Create multiple lines using matrix input to plot
plot1 = plot(X1,YMatrix1,'Parent',axes1);
set(plot1(1),'Marker','.','LineStyle','none','DisplayName','Experiment',...
    'Color',[0 0 0]);
set(plot1(2),'Color',[0 0 1],'DisplayName','Pseudo 1st order model');
set(plot1(3),'LineStyle','--','Color',[0 1 0],...
    'DisplayName','Pseudo 2nd order model');
set(plot1(4),'LineStyle','-.','Color',[1 0 0],'DisplayName','Avrami model');

% Create xlabel
xlabel('Time (sec)');

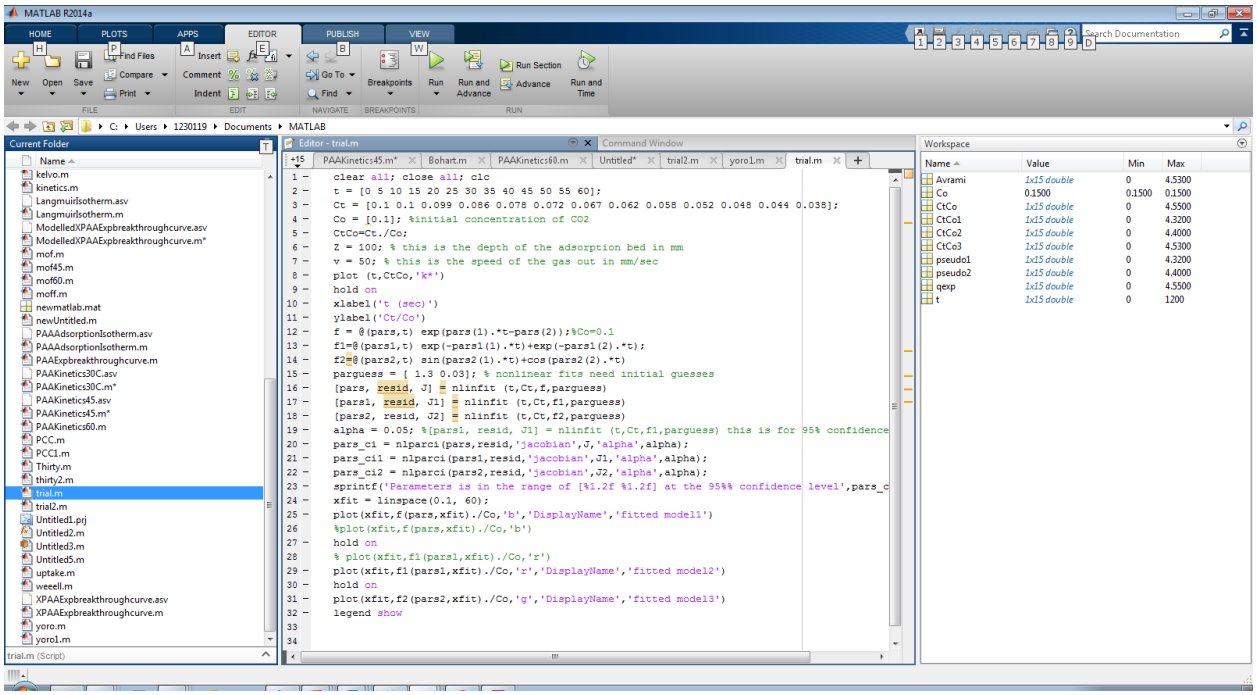
% Create ylabel
ylabel('q (mol/kg)');

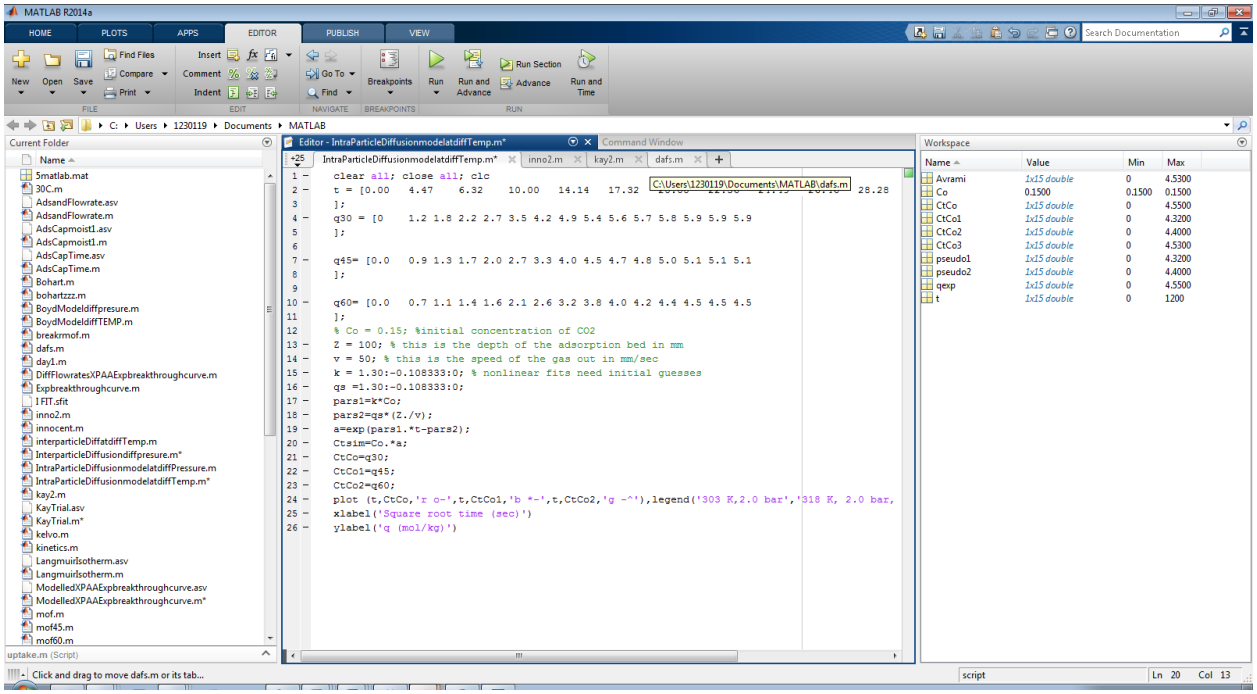
% Create legend
legend1 = legend(axes1,'show');
set(legend1,...
    'Position',[0.513988095238095 0.122619047619048 0.355357142857143 0.188888888888889])
```

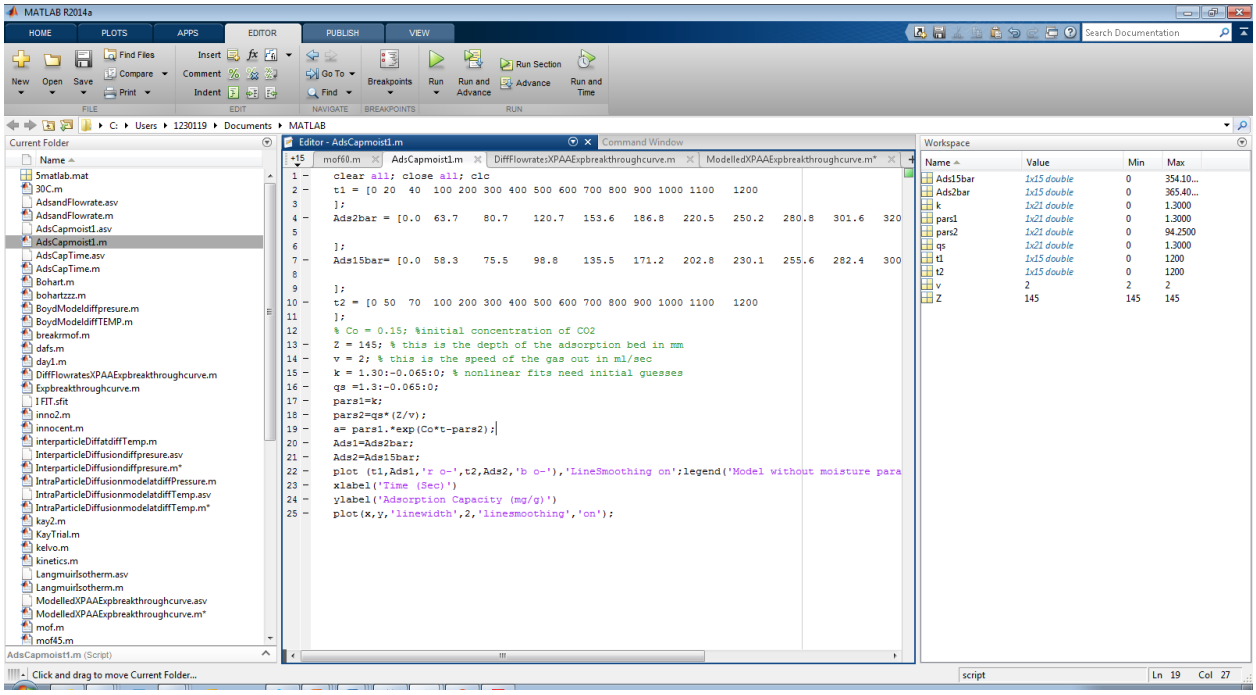


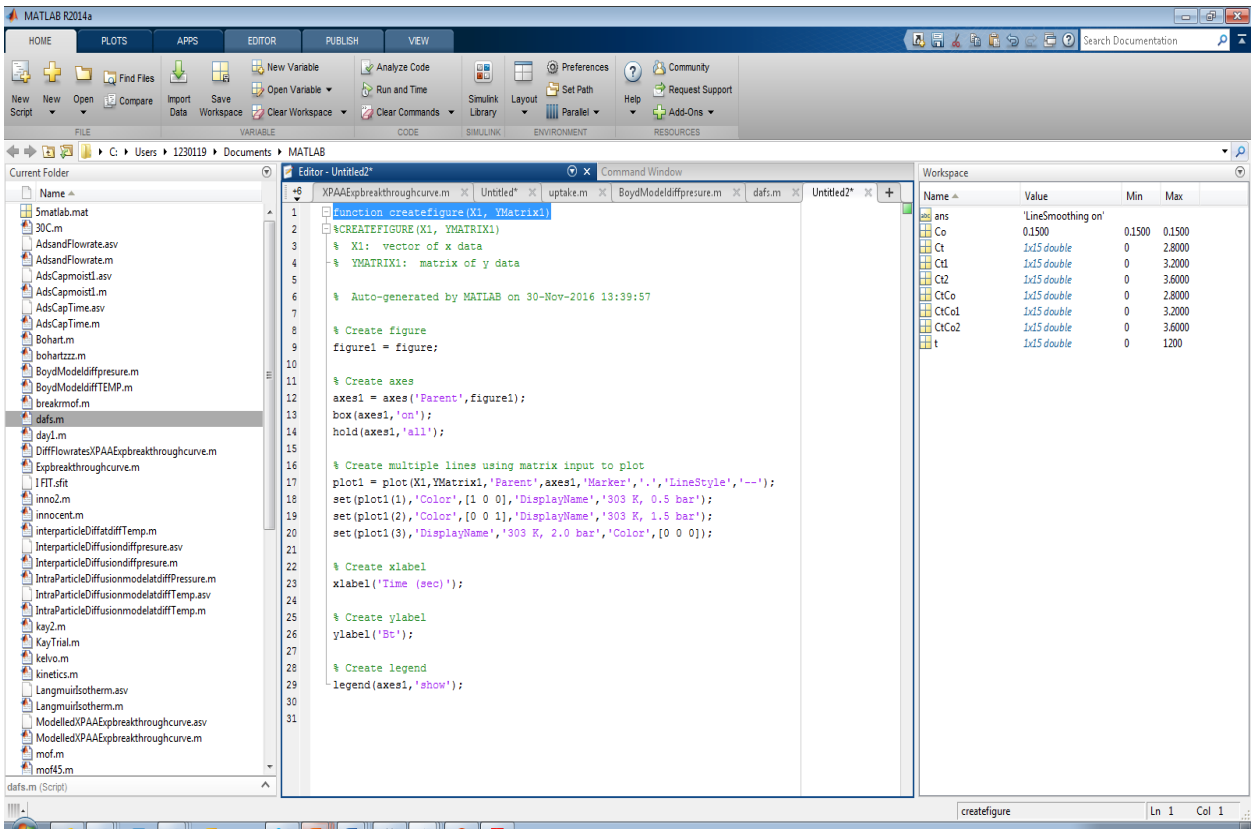

```
clear all; close all; clc
t = [0 5 10 15 20 25 30 35 40 45 50 55 60];
Ct1 = [0 0 0.001 0.014 0.022 0.028 0.033 0.038 0.042 0.048 0.052 0.056 0.062 ];
Co = 0.1; %initial concentration of CO2
CtCo=Ct./Co;
Z = 100; % this is the depth of the adsorption bed in mm
v = 50; % this is the speed of the gas out in mm/sec
h = 100; % this is the height of the adsorption bed in mm
u = 2.5; % this is the flowrate of the gas out in ml/sec
X = 0.1; % this is the mass of the adsorbent in grams
n = 3; % this is the number of experimental runs
plot (t,CtCo,'k*')
hold on
xlabel('t (sec)')
ylabel('Ct/Co')
f = @(pars,t) Co*(exp(pars(1))*(Co*t-pars(2)*z/v));%Co=0.1
% f1=@(pars1,t) Co(exp(pars1(1)*( (Co*t/(pars1(2)))-(h/u))));
% f2=@(pars2,t) Co(exp(pars2(1)-pars2(2)*t));
% f3=@(pars3,t) Co(exp(pars3(1)*(((pars3(2)*X)/u)-(Co*t)))+Co);
% f4=@(pars4,t) Co(exp(pars4(1)*t-pars4(2))/1+exp(pars4(1)*(t-pars4(2))));
% f5=@(pars5,t) Co/(pars5(1)-pars5(2)*t +1)^(1/n-1);
parguess = [ 1.3 0.3]; % nonlinear fits need initial guesses
[pars, resid, J] = nlinfit (t,Ct,f,parguess);
% [pars1, resid, J1] = nlinfit (t,Ct,f1,parguess);
% [pars2, resid, J2] = nlinfit (t,Ct,f2,parguess);
% [pars3, resid, J3] = nlinfit (t,Ct,f3,parguess);
% [pars4, resid, J4] = nlinfit (t,Ct,f4,parguess);
% [pars5, resid, J5] = nlinfit (t,Ct,f5,parguess);
alpha = 0.05; %[pars1, resid, J1] = nlinfit (t,Ct,f1,parguess) this is for 95% confidence
pars_ci = nlparci(pars,resid,'jacobian',J,'alpha',alpha);
% pars_ci1 = nlparci(pars1,resid,'jacobian',J1,'alpha',alpha);
% pars_ci2 = nlparci(pars2,resid,'jacobian',J2,'alpha',alpha);
% pars_ci3 = nlparci(pars3,resid,'jacobian',J3,'alpha',alpha);
% pars_ci4 = nlparci(pars4,resid,'jacobian',J4,'alpha',alpha);
```

Diffusion Models

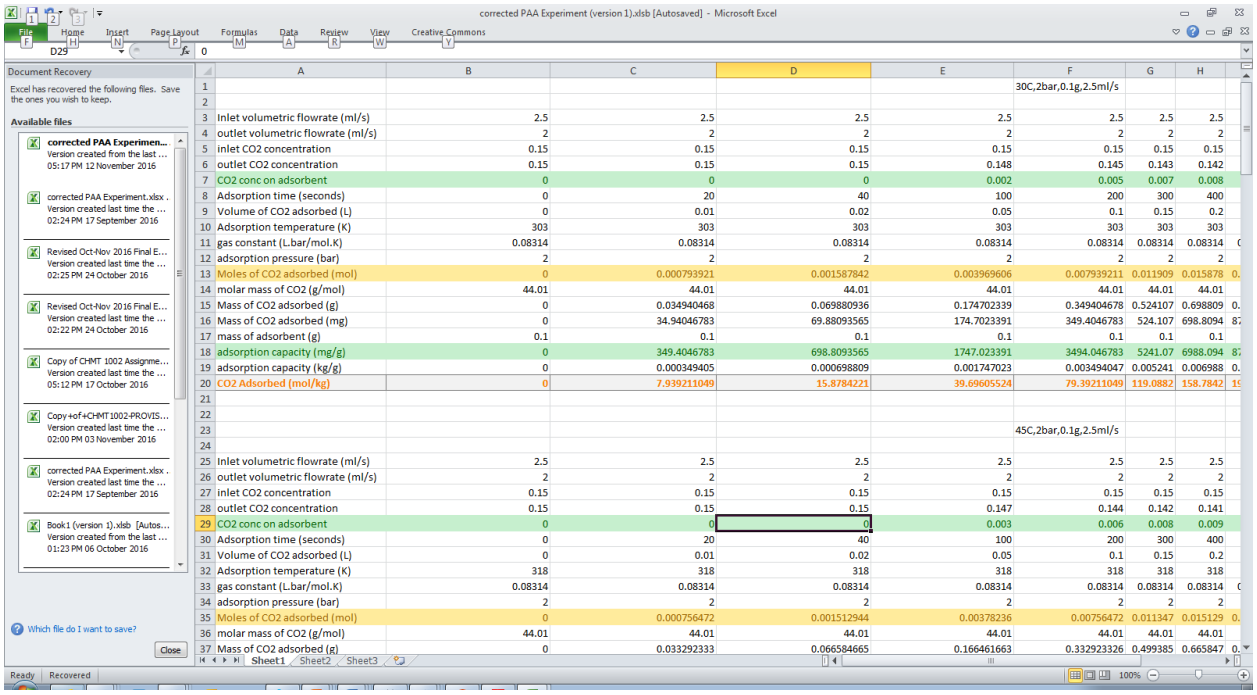





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Run Section
Advance
Run and Time
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BREAKPOINTS
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C: ▸ Users ▸ 1230119 ▸ Documents ▸ MATLAB
Current Folder
Name
5matlab.mat
30C.m
AdsandFlowrate.asv
AdsandFlowrate.m
AdsCapmoist1.asv
AdsCapmoist1.m
AdsCapTime.asv
AdsCapTime.m
Bohart.m
bohartzzz.m
BoydModeldiffpresure.m
BoydModeldiffTEMP.m
breakrmof.m
dafs.m
day1.m
DiffFlowratesXPAAExpbreakthroughcurve.m
Expbreakthroughcurve.m
FIT.sfit
inno2.m
innocent.m
interparticleDiffatdiffTemp.m
InterparticleDiffusiondiffpresure.asv
InterparticleDiffusiondiffpresure.m
IntraParticleDiffusionmodelatdiffPressure.m
IntraParticleDiffusionmodelatdiffTemp.asv
IntraParticleDiffusionmodelatdiffTemp.m
kay2.m
KayTrial.m
kelvo.m
kinetics.m
LangmuirIsotherm.asv
LangmuirIsotherm.m
ModelledXPAAExpbreakthroughcurve.asv
ModelledXPAAExpbreakthroughcurve.m
mof.m
mof45.m
AdsCapmoist1.m (Script)
Editor - AdsCapmoist1.m
mof60.m
AdsCapmoist1.m
DiffFlowrateXPAAExpbreakthroughcurve.m
ModelledXPAAExpbreakthroughcurve.m*
1 clear all; close all; clc
2 t1 = [0 20 40 100 200 300 400 500 600 700 800 900 1000 1100 1200
3];
4 Ads2bar = [0.0 63.7 80.7 120.7 153.6 186.8 220.5 250.2 280.8 301.6 320
5
6];
7 Ads15bar= [0.0 58.3 75.5 98.8 135.5 171.2 202.8 230.1 255.6 282.4 300
8
9];
10 t2 = [0 50 70 100 200 300 400 500 600 700 800 900 1000 1100 1200
11];
12 % Co = 0.15; %initial concentration of CO2
13 Z = 145; % this is the depth of the adsorption bed in mm
14 v = 2; % this is the speed of the gas out in ml/sec
15 k = 1.30:-0.065:0; % nonlinear fits need initial guesses
16 qs =1.3:-0.065:0;
17 pars1=k;
18 pars2=qs*(Z/v);
19 a= pars1.*exp(Co*t-pars2);
20 Ads1=Ads2bar;
21 Ads2=Ads15bar;
22 plot (t1,Ads1,'r o-',t2,Ads2,'b o-'),'LineSmoothing on';legend('Model without moisture para
23 xlabel('Time (Sec)')
24 ylabel('Adsorption Capacity (mg/g)')
25 plot(x,y,'linewidth',2,'linesmoothing','on');
Command Window
Workspace
Name
Value
Min
Max
Ads15bar 1x15 double 0 354.10...
Ads2bar 1x15 double 0 365.40...
k 1x21 double 0 1.3000
pars1 1x21 double 0 1.3000
pars2 1x21 double 0 94.2500
qs 1x21 double 0 1.3000
t1 1x15 double 0 1200
t2 1x15 double 0 1200
v 2 2 2
Z 145 145 145
Click and drag to move Current Folder...
script
Ln 19 Col 27

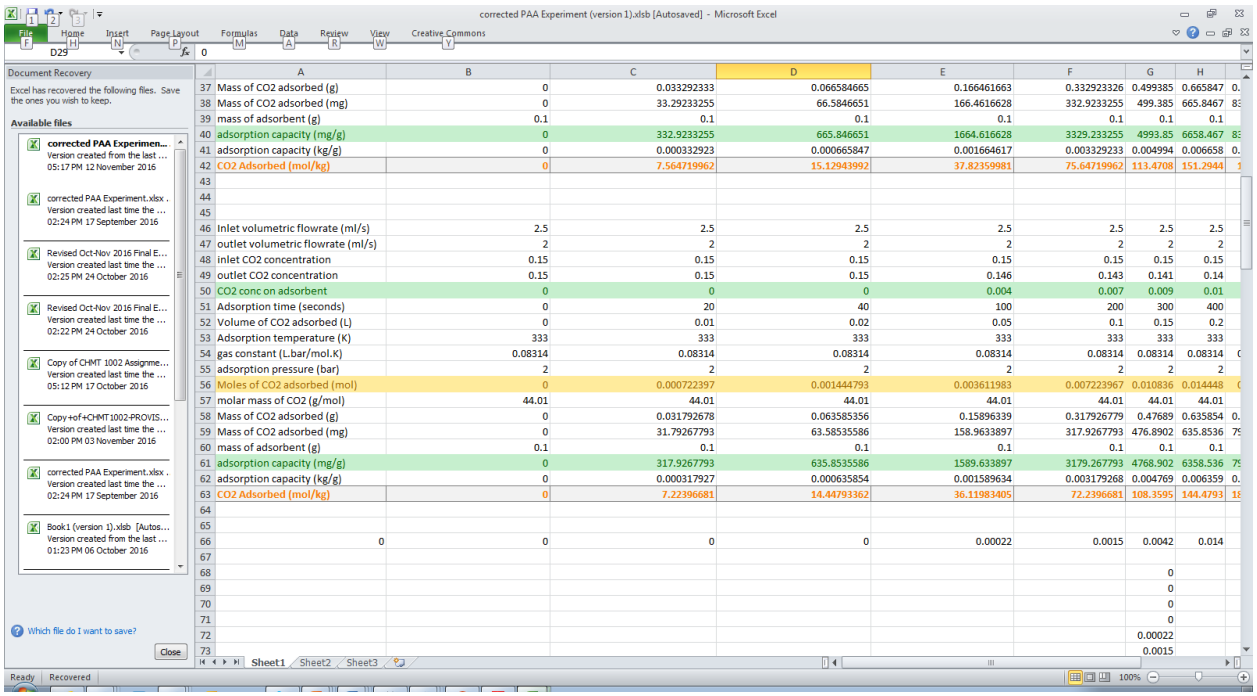

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Run and Time
Clear Commands
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Layout
Preferences
Set Path
Parallel
Help
Community
Request Support
Add-Ons
FILE
VARIABLE
CODE
SIMULINK
ENVIRONMENT
RESOURCES
C: ▸ Users ▸ 1230119 ▸ Documents ▸ MATLAB
Current Folder
Name
5matlab.mat
30C.m
AdsandFlowrate.asv
AdsandFlowrate.m
AdsCapmoist1.asv
AdsCapmoist1.m
AdsCapTime.asv
AdsCapTime.m
Bohart.m
bohartzzz.m
BoydModeldiffpresure.m
BoydModeldiffTEMP.m
breakrmof.m
dafs.m
day1.m
DiffFlowratesXPAAExpbreakthroughcurve.m
Expbreakthroughcurve.m
FIT.sfit
inno2.m
innocent.m
interparticleDiffatdiffTemp.m
InterparticleDiffusiondiffpresure.asv
InterparticleDiffusiondiffpresure.m
IntraParticleDiffusionmodelatdiffPressure.m
IntraParticleDiffusionmodelatdiffTemp.asv
IntraParticleDiffusionmodelatdiffTemp.m
kay2.m
KayTrial.m
kelvo.m
kinetics.m
LangmuirIsotherm.asv
LangmuirIsotherm.m
ModelledXPAAExpbreakthroughcurve.asv
ModelledXPAAExpbreakthroughcurve.m
mof.m
mof45.m
dafs.m (Script)
Editor - Untitled2*
XPAAExpbreakthroughcurve.m
Untitled*
uptake.m
BoydModeldiffpresure.m
dafs.m
Untitled2*
1 function createfigure(X1, YMatrix1)
2 %CREATEFIGURE(X1, YMATRIX1)
3 % X1: vector of x data
4 % YMATRIX1: matrix of y data
5
6 % Auto-generated by MATLAB on 30-Nov-2016 13:39:57
7
8 % Create figure
9 figure1 = figure;
10
11 % Create axes
12 axes1 = axes('Parent',figure1);
13 box(axes1,'on');
14 hold(axes1,'all');
15
16 % Create multiple lines using matrix input to plot
17 plot1 = plot(X1,YMatrix1,'Parent',axes1,'Marker','.','LineStyle','--');
18 set(plot1(1),'Color',[1 0 0],'DisplayName','303 K, 0.5 bar');
19 set(plot1(2),'Color',[0 0 1],'DisplayName','303 K, 1.5 bar');
20 set(plot1(3),'DisplayName','303 K, 2.0 bar','Color',[0 0 0]);
21
22 % Create xlabel
23 xlabel('Time (sec)');
24
25 % Create ylabel
26 ylabel('Bt');
27
28 % Create legend
29 legend(axes1,'show');
30
31
Command Window
Workspace
Name
Value
Min
Max
ans 'LineSmoothing on'
Co 0.1500 0.1500 0.1500
Ct 1x15 double 0 2.8000
Ct1 1x15 double 0 3.2000
Ct2 1x15 double 0 3.6000
CtCo 1x15 double 0 2.8000
CtCo1 1x15 double 0 3.2000
CtCo2 1x15 double 0 3.6000
t 1x15 double 0 1200
createfigure
Ln 1 Col 1

APPENDIX B: EXPERIMENTAL DATA



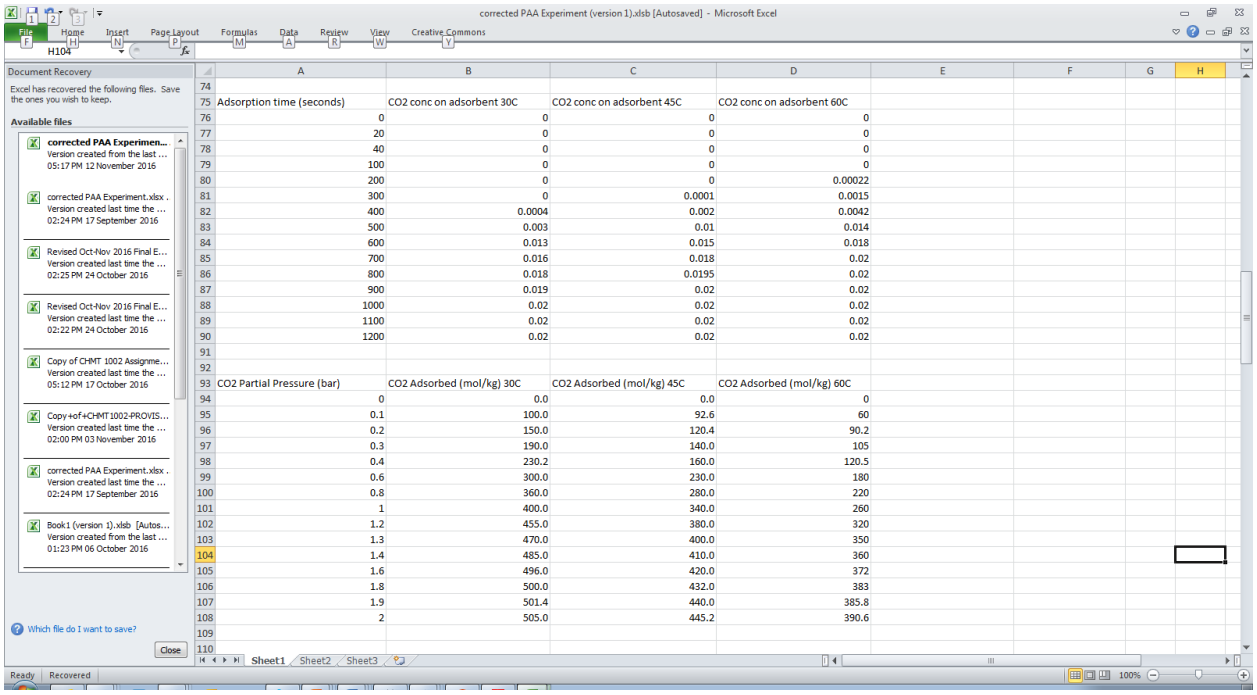
corrected PAA Experiment (version 1).xlsb [Autosaved] - Microsoft Excel

	A	B	C	D	E	F	G	H
1						30C,2bar,0.1g,2.5ml/s		
2								
3	Inlet volumetric flowrate (ml/s)	2.5	2.5	2.5	2.5	2.5	2.5	2.5
4	outlet volumetric flowrate (ml/s)	2	2	2	2	2	2	2
5	inlet CO2 concentration	0.15	0.15	0.15	0.15	0.15	0.15	0.15
6	outlet CO2 concentration	0.15	0.15	0.15	0.148	0.145	0.143	0.142
7	CO2 conc on adsorbent	0	0	0	0.002	0.005	0.007	0.008
8	Adsorption time (seconds)	0	20	40	100	200	300	400
9	Volume of CO2 adsorbed (L)	0	0.01	0.02	0.05	0.1	0.15	0.2
10	Adsorption temperature (K)	303	303	303	303	303	303	303
11	gas constant (L.bar/mol.K)	0.08314	0.08314	0.08314	0.08314	0.08314	0.08314	0.08314
12	adsorption pressure (bar)	2	2	2	2	2	2	2
13	Moles of CO2 adsorbed (mol)	0	0.000793921	0.001587842	0.003969606	0.007939211	0.011909	0.015878
14	molar mass of CO2 (g/mol)	44.01	44.01	44.01	44.01	44.01	44.01	44.01
15	Mass of CO2 adsorbed (g)	0	0.034940468	0.069880936	0.174702339	0.349404678	0.524107	0.698809
16	Mass of CO2 adsorbed (mg)	0	34.94046783	69.88093565	174.7023391	349.4046783	524.107	698.8094
17	mass of adsorbent (g)	0.1	0.1	0.1	0.1	0.1	0.1	0.1
18	adsorption capacity (mg/g)	0	349.4046783	698.8093565	1747.023391	3494.046783	5241.07	6988.094
19	adsorption capacity (kg/g)	0	0.000349405	0.000698809	0.001747023	0.003494047	0.005241	0.006988
20	CO2 Adsorbed (mol/kg)	0	7.939211049	15.8784221	39.69605524	79.39211049	119.0882	158.7842
21								
22								
23						45C,2bar,0.1g,2.5ml/s		
24								
25	Inlet volumetric flowrate (ml/s)	2.5	2.5	2.5	2.5	2.5	2.5	2.5
26	outlet volumetric flowrate (ml/s)	2	2	2	2	2	2	2
27	inlet CO2 concentration	0.15	0.15	0.15	0.15	0.15	0.15	0.15
28	outlet CO2 concentration	0.15	0.15	0.15	0.147	0.144	0.142	0.141
29	CO2 conc on adsorbent	0	0	0	0.003	0.006	0.008	0.009
30	Adsorption time (seconds)	0	20	40	100	200	300	400
31	Volume of CO2 adsorbed (L)	0	0.01	0.02	0.05	0.1	0.15	0.2
32	Adsorption temperature (K)	318	318	318	318	318	318	318
33	gas constant (L.bar/mol.K)	0.08314	0.08314	0.08314	0.08314	0.08314	0.08314	0.08314
34	adsorption pressure (bar)	2	2	2	2	2	2	2
35	Moles of CO2 adsorbed (mol)	0	0.000756472	0.001512944	0.00378236	0.00756472	0.011347	0.015129
36	molar mass of CO2 (g/mol)	44.01	44.01	44.01	44.01	44.01	44.01	44.01
37	Mass of CO2 adsorbed (g)	0	0.033292333	0.066584665	0.166461663	0.332923326	0.499385	0.665847

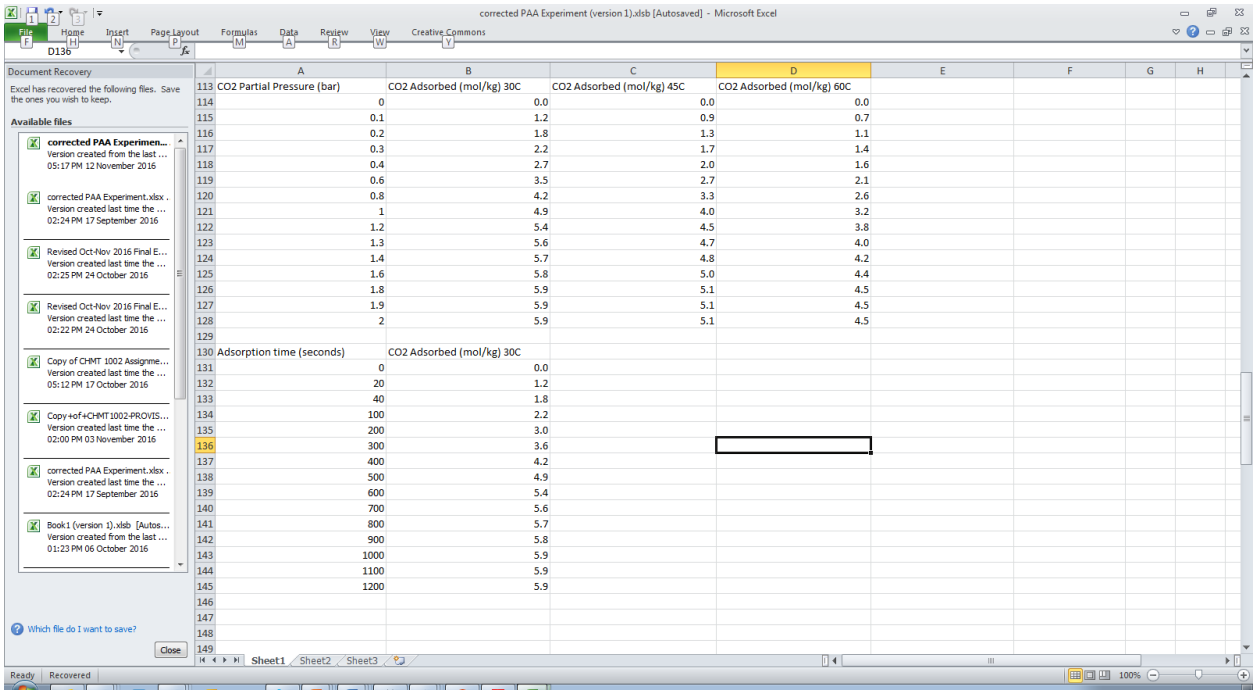


corrected PAA Experiment (version 1).xlsb [Autosaved] - Microsoft Excel

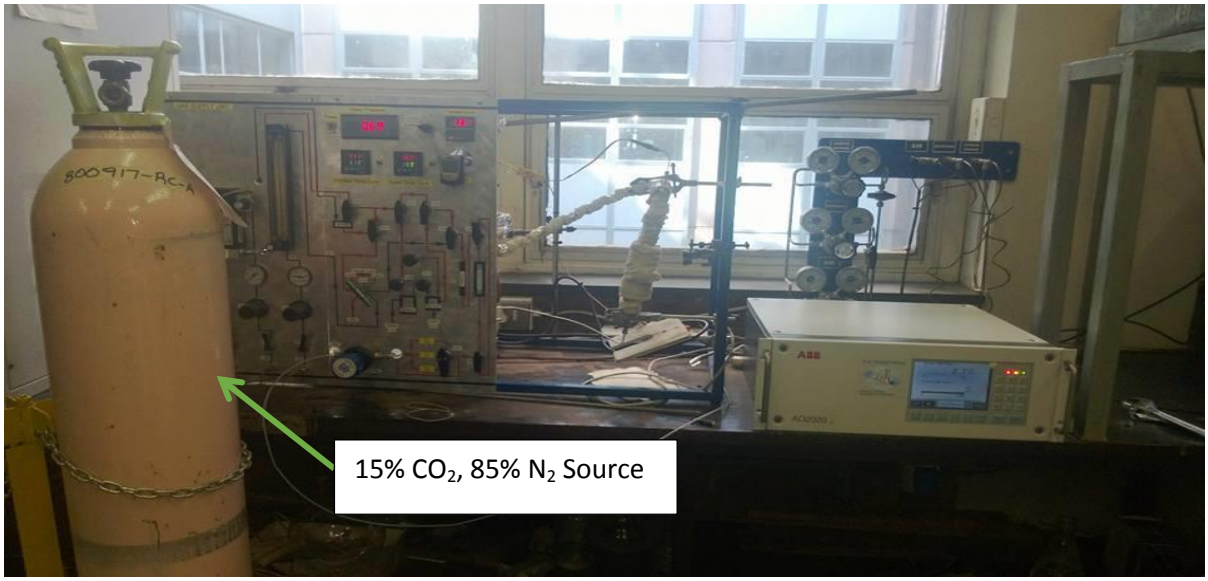
	A	B	C	D	E	F	G	H
37	Mass of CO2 adsorbed (g)	0	0.033292333	0.066584665	0.166461663	0.332923326	0.499385	0.665847
38	Mass of CO2 adsorbed (mg)	0	33.29233255	66.5846651	166.4616628	332.9233255	499.385	665.8467
39	mass of adsorbent (g)	0.1	0.1	0.1	0.1	0.1	0.1	0.1
40	adsorption capacity (mg/g)	0	332.9233255	665.846651	1664.616628	3329.233255	4993.85	6658.467
41	adsorption capacity (kg/g)	0	0.000332923	0.000665847	0.001664617	0.003329233	0.004994	0.006658
42	CO2 Adsorbed (mol/kg)	0	7.564719962	15.12943992	37.82359981	75.64719962	113.4708	151.2944
43								
44								
45								
46	Inlet volumetric flowrate (ml/s)	2.5	2.5	2.5	2.5	2.5	2.5	2.5
47	outlet volumetric flowrate (ml/s)	2	2	2	2	2	2	2
48	inlet CO2 concentration	0.15	0.15	0.15	0.15	0.15	0.15	0.15
49	outlet CO2 concentration	0.15	0.15	0.15	0.146	0.143	0.141	0.14
50	CO2 conc on adsorbent	0	0	0	0.004	0.007	0.009	0.01
51	Adsorption time (seconds)	0	20	40	100	200	300	400
52	Volume of CO2 adsorbed (L)	0	0.01	0.02	0.05	0.1	0.15	0.2
53	Adsorption temperature (K)	333	333	333	333	333	333	333
54	gas constant (L.bar/mol.K)	0.08314	0.08314	0.08314	0.08314	0.08314	0.08314	0.08314
55	adsorption pressure (bar)	2	2	2	2	2	2	2
56	Moles of CO2 adsorbed (mol)	0	0.000722397	0.001444793	0.003611983	0.007223967	0.010836	0.014448
57	molar mass of CO2 (g/mol)	44.01	44.01	44.01	44.01	44.01	44.01	44.01
58	Mass of CO2 adsorbed (g)	0	0.031792678	0.063585356	0.15896339	0.317926779	0.47689	0.635854
59	Mass of CO2 adsorbed (mg)	0	31.79267793	63.58535586	158.9633897	317.9267793	476.8902	635.8536
60	mass of adsorbent (g)	0.1	0.1	0.1	0.1	0.1	0.1	0.1
61	adsorption capacity (mg/g)	0	317.9267793	635.8535586	1589.633897	3179.267793	4768.902	6358.536
62	adsorption capacity (kg/g)	0	0.000317927	0.000635854	0.001589634	0.003179268	0.004769	0.006359
63	CO2 Adsorbed (mol/kg)	0	7.22396681	14.44793362	36.11983405	72.2396681	108.3595	144.4793
64								
65								
66	0	0	0	0	0.00022	0.0015	0.0042	0.014
67								
68							0	
69							0	
70							0	
71							0	
72							0.00022	
73							0.0015	

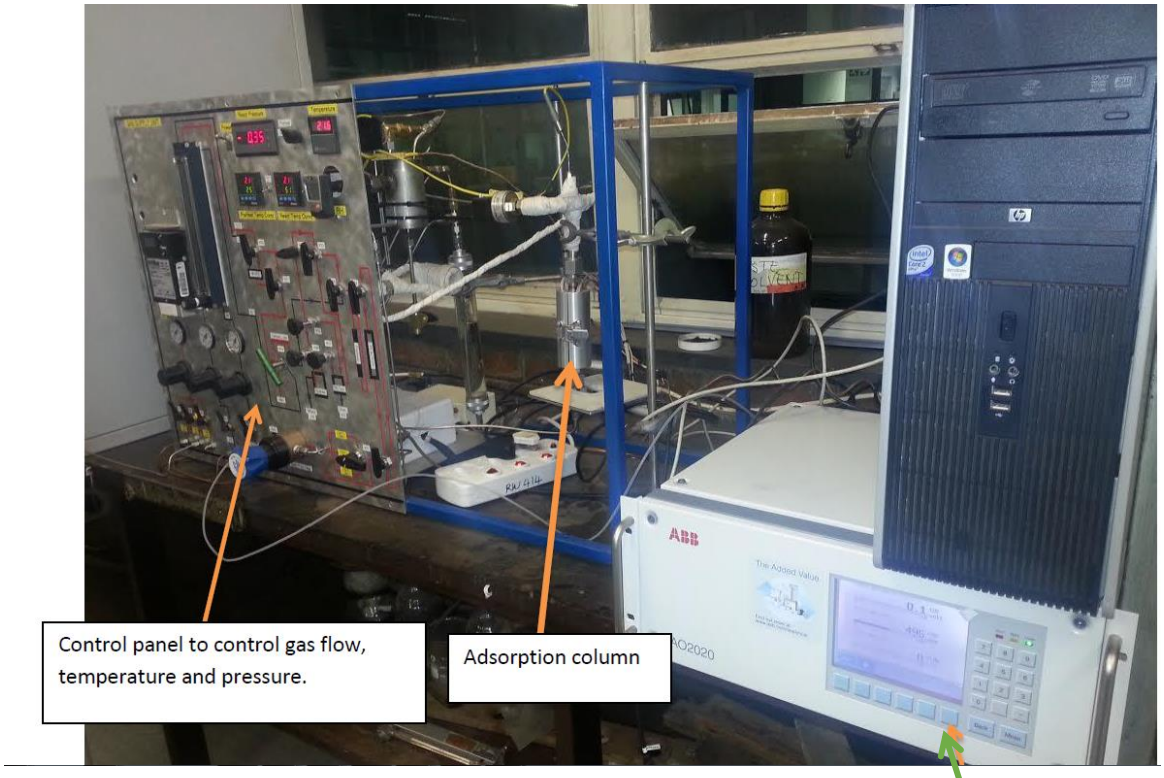


	A	B	C	D
75	Adsorption time (seconds)	CO2 conc on adsorbent 30C	CO2 conc on adsorbent 45C	CO2 conc on adsorbent 60C
76	0	0	0	0
77	20	0	0	0
78	40	0	0	0
79	100	0	0	0
80	200	0	0	0.00022
81	300	0	0.0001	0.0015
82	400	0.0004	0.002	0.0042
83	500	0.003	0.01	0.014
84	600	0.013	0.015	0.018
85	700	0.016	0.018	0.02
86	800	0.018	0.0195	0.02
87	900	0.019	0.02	0.02
88	1000	0.02	0.02	0.02
89	1100	0.02	0.02	0.02
90	1200	0.02	0.02	0.02
91				
92				
93	CO2 Partial Pressure (bar)	CO2 Adsorbed (mol/kg) 30C	CO2 Adsorbed (mol/kg) 45C	CO2 Adsorbed (mol/kg) 60C
94	0	0.0	0.0	0
95	0.1	100.0	92.6	60
96	0.2	150.0	120.4	90.2
97	0.3	190.0	140.0	105
98	0.4	230.2	160.0	120.5
99	0.6	300.0	230.0	180
100	0.8	360.0	280.0	220
101	1	400.0	340.0	260
102	1.2	455.0	380.0	320
103	1.3	470.0	400.0	350
104	1.4	485.0	410.0	360
105	1.6	496.0	420.0	372
106	1.8	500.0	432.0	383
107	1.9	501.4	440.0	385.8
108	2	505.0	445.2	390.6
109				
110				



	A	B	C	D
113	CO2 Partial Pressure (bar)	CO2 Adsorbed (mol/kg) 30C	CO2 Adsorbed (mol/kg) 45C	CO2 Adsorbed (mol/kg) 60C
114	0	0.0	0.0	0.0
115	0.1	1.2	0.9	0.7
116	0.2	1.8	1.3	1.1
117	0.3	2.2	1.7	1.4
118	0.4	2.7	2.0	1.6
119	0.6	3.5	2.7	2.1
120	0.8	4.2	3.3	2.6
121	1	4.9	4.0	3.2
122	1.2	5.4	4.5	3.8
123	1.3	5.6	4.7	4.0
124	1.4	5.7	4.8	4.2
125	1.6	5.8	5.0	4.4
126	1.8	5.9	5.1	4.5
127	1.9	5.9	5.1	4.5
128	2	5.9	5.1	4.5
129				
130	Adsorption time (seconds)	CO2 Adsorbed (mol/kg) 30C		
131	0	0.0		
132	20	1.2		
133	40	1.8		
134	100	2.2		
135	200	3.0		
136	300	3.6		
137	400	4.2		
138	500	4.9		
139	600	5.4		
140	700	5.6		
141	800	5.7		
142	900	5.8		
143	1000	5.9		
144	1100	5.9		
145	1200	5.9		
146				
147				
148				
149				


15% CO_2, 85% N_2 Source


Control panel to control gas flow, temperature and pressure.
Adsorption column
ABB Gas Analyser

APPENDIX C: PUBLISHED WORKS



environments

MDPI

Review

The Potential of CO_2 Capture and Storage Technology in South Africa's Coal-Fired Thermal Power Plants

Kelvin O. Yoro * and Patrick T. Sekoai

Sustainable Energy & Environment Research Unit, Faculty of Engineering and the Built Environment, School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg 2050, South Arica; patrick.sekoai1@students.wits.ac.za

* Correspondence: kelvin.yoro1@students.wits.ac.za; Tel.: +27-74-299-5917

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Abstract: The global atmospheric concentration of anthropogenic gases, such as carbon dioxide, has increased substantially over the past few decades due to the high level of industrialization and urbanization that is occurring in developing countries, like South Africa. This has escalated the challenges of global warming. In South Africa, carbon capture and storage (CCS) from coal-fired power plants is attracting increasing attention as an alternative approach towards the mitigation of carbon dioxide emission. Therefore, innovative strategies and process optimization of CCS systems is essential in order to improve the process efficiency of this technology in South Africa. This review assesses the potential of CCS as an alternative approach to reducing the amount CO_2 emitted from the South African coal-fired power plants. It examines the various CCS processes that could be used for capturing the emitted CO_2. Finally, it proposes the use of new adsorbents that could be incorporated towards the improvement of CCS technology.

Keywords: CO_2 capture and storage; climate change; coal-fired power plants; South Africa

1. Introduction

Over the past decade, global carbon dioxide emissions have significantly increased by approximately 2.7%, which is 60% more than that of the late 20th century [1]. South Africa is among the countries that are highly affected by carbon emissions; the country is the leading CO_2 emitter in Africa and is ranked amongst the top twelve emitters in the world [2]. The country's emissions are intensified by the energy and manufacturing sectors, which release huge amounts of CO_2 into the atmosphere. For instance, an estimated 367.6 million tons of CO_2 were emitted by South Africa in 2011; this value increased to 476 million tons in 2015. Most of the country's CO_2 emissions are derived from the burning of coal [3]. Thus, future projections show that carbon emissions will continue to increase unless there is acceleration in the formation of carbon-neutral technologies that will reduce this problem or incorporate CO_2 capture technologies from major emitting sources, such as the coal-fired thermal power plants.

Moreover, there has been a significant decline in the country's agricultural output due to low rainfall seasons and temperature rise, which is caused by climate change [4]. Many parts of South Africa are experiencing drought and are therefore no longer suitable for commercial farming. Studies have reported that carbon emissions if not curtailed will have the following devastating effects: (i) South Africa's coastal region is expected to have an atmospheric temperature rise of 2 °C by 2050 and 4 °C by 2100; (ii) the country's interior region is also expected to increase by 4 °C in 2050 and 7 °C in 2100; (iii) this will affect the country's food security; (iv) alien invasive plants might increase and negatively affect the country's water resources; (v) this will likely exacerbate health issues due to droughts and floods; diseases, such as malaria and cholera, have been linked to extreme weather

patterns; and (vi) bushlands and various commercial plantations will be vulnerable to wildfires [4]. It is estimated that in order to reduce global warming or limit global average temperatures by 2 °C in 2050, global CO_2 emissions should be reduced by at least 50% [5]. Currently, a range of options that could help to mitigate climate change are being considered worldwide, including carbon capture and storage technology (CCS) [6]. CCS technology can contribute towards the reduction of carbon emissions, thus allowing the continual use of coal-dependent energy markets, like South Africa. The aim of CCS is to capture carbon emissions from point sources, such as coal-fired power plants and industrial processes, to prevent it from being released into the atmosphere [7]. The captured CO_2 can be used for enhanced oil recovery; it can be utilized in chemical and beverage industries for the preservation of drinks. Alternatively, it can be stored in underground rocks or deep ocean waters [8]. Devilliers et al. [9] highlighted that South Africa's economy is primarily dependent on coal reserves for energy supply, and therefore, its utilization is envisaged to continue for the next three decades. In addition, 75% of the country's primary energy supply and 93% of the electricity are derived from coal reserves. The drawback about coal reserves is that they are escalating the country's CO_2 emissions and consequently contributing to environmental degradation, i.e., more than 80% of the country's carbon footprint is produced from the coal-fired power plants [10,11].

The integration of clean and sustainable energy technologies in South Africa requires solutions that deal with high CO_2-emitting sources, such as coal-fired thermal power plants [12]. This implies that sustainability assessment of CCS technology is an important aspect of climate policy, especially in highly industrialized countries, like South Africa [13]. Nonetheless, CCS has some technical and economic barriers that must be addressed before it can be implemented on the industrial scale, which include high capital incentives and leakage problems. CCS is also hindered by economic, social and legal barriers [14]. Besides, some countries have limited geological storage capacity for CO_2 capture [15]. The development of CCS is still in its infancy in South Africa, implying that there are no frameworks for this technology [16]. Against this background, this review examines the potential of CCS technology for mitigating CO_2 emitted from coal-fired thermal power plants in South Africa. It investigates the various CCS methods that could be applied to capture the CO_2 generated from these coal-fired power plants. Lastly, it recommends the use of new adsorbents that could be utilized towards the implementation of CCS systems in South African coal-fired thermal power plants and also the retrofitting of capture devices into the existing coal-fired thermal power plants.

2. Technological Routes for CO_2 Capture

The efficient capture of anthropogenic CO_2 emitted from large point sources such as power plants, is seen as an important strategy that can be used to significantly reduce the level of atmospheric CO_2. This is because the generation of CO_2 is inherent in the combustion of hydrocarbon fuels, which is a daily occurrence in South Africa's coal-fired thermal power plants [17–28]. Currently, pre-combustion, post-combustion and oxy-fuel combustion captures are the three basic technological routes used to capture CO_2 [29–36]. These technological routes are discussed below on a broader note and related to their possible implementation in South African coal-fired thermal power plants.

2.1. Post-Combustion

This capture technology involves the separation of CO_2 from waste gas streams after the conversion of the carbon source of CO_2 [37–40]. This method is very effective at capturing CO_2 from power plants. It is also known as post-conversion capture, but when applied in power plants, it is referred to as post-combustion capture [41]. The post-combustion method of CO_2 capture includes solvent absorption, solid sorbent adsorption, membranes and cryogenic separation [42,43]. Out of all of these options, CO_2 absorption by monoethanolamine is extensively used and referred to as a very mature technology [44]. The post-combustion capture is still considered as the most mature capture route, because it has a good reputation within many industrial applications and also a better operational flexibility [45–48]. The post-combustion capture technology is mostly used in power

plants because it has the possibility of retrofitting in existing power plants, such as the South African coal-fired thermal power plants. The South African energy sector is mainly driven by coal, and the sustainable use of coal in these power plants must continue in order to avoid escalating the price of electricity. On this note, retrofitting CO_2 capture devices in the already existing coal-fired power plants in South Africa becomes a viable option in order to curtail CO_2 emission to the atmosphere. Since the post-combustion technology allows for possible retrofitting, it becomes a promising technology that can be implemented in the South African coal-fired thermal power plants with no associated increase in the price of electricity, because coal will still remain the primary source of electricity in the country, and carbon emissions from this sector will be reduced drastically.

2.2. Pre-Combustion

The pre-combustion capture refers to capturing CO_2 generated as an undesired co-product of a conversion process [49–54]. In the pre-combustion capture, fuel from the power plant is reacted with oxygen to generate a syngas mixture, which is carried out in the gasification step [55–60]. Carbon dioxide is then reacted with steam in the second step to produce CO_2 and H_2 before the CO_2 is finally separated using a physical or chemical absorption process [61–65]. The pre-combustion capture technique incurs high costs for chemical solvent regeneration. However, for physical solvents, the costs are lower because they are regenerated by pressure reduction instead of using heat. Physical solvents are most suitable for use at high operating pressure and low temperatures, and it is more efficient when the CO_2 streams in the power plants are more concentrated [66–70]. In the context of CO_2 capture from the South African coal-fired power plants, the pre-combustion technology cannot be fully implemented because it has a high energy requirement with no option of retrofitting capture devices into existing power plants. This invariably means that the implementation of this technology will only be feasible in newly-built power plants and cannot be implemented in the already existing coal-fired thermal power plants in South Africa. This makes the pre-combustion CO_2 capture technology more expensive and difficult to implement in the South African power sector.

2.3. Oxy-Fuel

In the oxy-fuel combustion technological approach for CO_2 capture, flue gas consisting of pure oxygen is burnt. This technological route produces a flue gas stream that is highly saturated with CO_2 [71–76]. This technology also produces flame with an excessively high temperature because, theoretically, if fossil fuel (coal) is burnt in pure oxygen, much heat is produced [77–89]. The pure oxygen is produced by cryogenics. This technique is a modification of the pulverized coal-fired power plant in South Africa. It involves burning coal in nearly pure oxygen. The main advantage of the oxy-fuel CO_2 capture technique is that the flue gas is available at a high CO_2 concentration of approximately 75.7 mol%, thereby reducing compression costs and facilitating efficient CO_2 removal [90–104]. Although this technology appears promising if implemented for CO_2 capture in power plants, its possibility of implementation in the South African coal-fired power plants is quite slim because burning coal in pure oxygen instead of air on a large scale is very expensive. This will in turn increase the cost of electricity in South Africa. Therefore, it is not a suitable technological route for CO_2 capture in South Africa.

3. Separation Technologies during Post-Combustion CO_2 Capture

The preference of one technological route over others could be attributed to its ease of access, its possibility of the capture process, retrofitting to existing power plants, the maturity level of such a technological route and the period needed for the implementation of such technology [105]. Currently, there is a wide range of CO_2 capture and separation techniques from gas streams, which could be implemented in the South African coal-fired thermal power plants. They are based on physical and chemical processes, which include adsorption, absorption, cryogenic and membrane separation technologies. They are discussed below.

3.1. Cryogenic Separation

The cryogenic separation method for CO_2 capture is mainly based on the principle of condensation and cooling [106–110]. It is mostly applied in CO_2 capture systems where the gas streams contain a high concentration of CO_2. The challenge about cryogenic separation is that it cannot be used in CO_2 capture from power plants because the power plants have a more dilute CO_2 stream [111,112]. Another setback is that this technology is energy intensive, i.e., it requires high amounts of energy for CO_2 separation. The concentration of CO_2 from South African coal-fired power plants is quite low, thereby rendering this CO_2 separation method difficult to implement in South Africa. Furthermore, cryogenic separation is best carried out at very low temperatures [113–119]. However, it is difficult to attain very low temperatures in coal-fired power plants that will be suitable for CO_2 capture using this technique. In most cryogenic separation processes, various components in gas mixtures are separated by a series of compression, refrigeration and separation steps [120]. Impurities lower the phase transition temperature of CO_2 in cryogenic separation processes to as low as -80 °C. In this case, the refrigeration energy penalty increases substantially, and there is a huge possibility of CO_2 frost formation, which is a threat to equipment safety [120–123]. As a result, another technology that is economically viable and less energy intensive needs to be investigated.

3.2. Membrane Separation

Corti et al. [65] investigated CO_2 capture using membranes and concluded that the application of CO_2 capture from flue gases using membranes can only be competitive if the CO_2 concentration in the flue gas is higher than 10%. CO_2 capture using membranes operates on the principle of differences in the physical or chemical interaction between the CO_2 gas and the membrane for which the membrane is designed in such a way as to allow one gas to pass through faster than the other. The membrane modules can also be used as a gas absorption column or as a conventional membrane separation unit [124–128]. Although the membrane technology is relatively new, it requires high energy during separation, and it is widely known for its poor selectivity [129–135]. This poses a major disadvantage for CO_2 capture using membranes [136–138]. More so, this technology uses either inorganic ceramic membranes or organic polymeric membranes [139,140]. Ceramic membranes are quite expensive; however, it is very difficult to achieve a high degree of separation of CO_2 and a high purity of CO_2 at the same time with CO_2 in the flue gas through a single-stage ceramic or polymeric membrane. This is another major limitation of this CO_2 capture technology. This technology for post-combustion CO_2 capture is not suitable for implementation in the South African coal-fired power plants owing to its expensive nature if ceramic membranes are used and fouling in the case of polymeric membranes. Although the polymeric membranes have excellent selectivity and permeability for CO_2 capture, they have very low thermal stability and these membranes may be plasticized with the influence of CO_2 in the membrane. Therefore, application of the membrane technology for post-combustion CO_2 capture in power plants similar to the South African coal-fired thermal power plants is limited. Efficient capture technologies for CO_2 with low cost and high CO_2 capture potential, as well as selectivity need to be studied further as an alternative to the use of membranes for post-combustion CO_2 capture [141].

3.3. Absorption

The absorption technology involves the use of chemical solvents to capture CO_2. It is a well-researched, robust, mature technology, and it is widely applied industrially. It is sub-divided into physical and chemical absorption. The former is temperature and pressure dependent, and the absorption of CO_2 from the flue gas occurs at high pressure and low temperature. Whereas in the latter, the absorption of CO_2 from the flue gas depends on the acid-base neutralization reaction using basic solvents [142–145]. The most commonly-used solvents for absorption of CO_2 from flue gases are basically amines [146], chilled methanol [147] and ammonia solution [148]. Even though the absorption technology is considered as a mature technology for CO_2 capture, the use of solvents for

this technology makes it corrosive and energy intensive due to high energy demands during solvent regeneration, and it is also expensive. The major limitation of this technique is that it uses liquid absorbents, which corrode piping in power plants; as such, it is not very suitable for adoption in the South African coal-fired power plants. Consequently, the adsorption technology that uses solid adsorbents for CO_2 capture is highly recommended for use in most South-African coal-fired power plants because it is not corrosive, the least expensive and has minimum energy requirements for the regeneration of the solid adsorbents [149]. Liquids, such as monoethanolamine, react readily with CO_2, but because heat must be applied to remove CO_2 from the resulting liquid, the process is not economically viable for implementation in power plants. If the approach were applied to every power station in the South Africa, CO_2 capture could cost 30% of the country's growth in gross domestic product each year [150]. Less expensive methods for capturing CO_2 and hydrocarbon emissions with minimal energy costs need to be investigated.

In order to reduce the high thermal energy consumption in the power plants, the concentration of monoethanolamine used during the post-combustion CO_2 capture process should be increased, and better corrosion inhibitors should be used to eliminate the high corrosive effect of monoethanolamine as a solvent for the CO_2 capture by absorption. Figure 1 shows a summary of various CO_2 capture and separation technologies for post-combustion CO_2 capture.

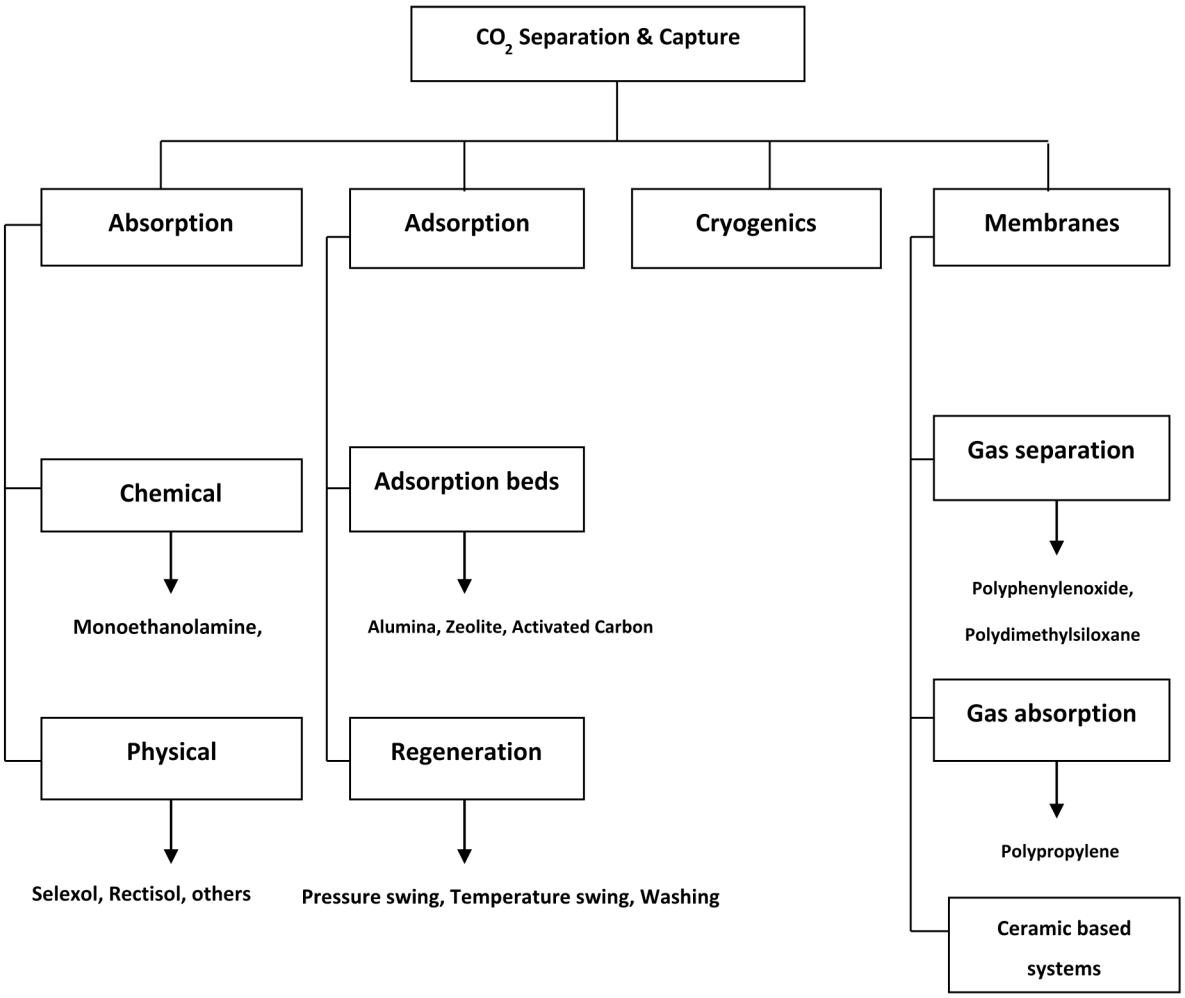


Figure 1. Different CO_2 separation and capture technologies for post-combustion CO_2 capture [82].

3.4. Adsorption

This technology is extensively used in chemical and environmental processes. It uses various adsorbents such as zeolites, activated carbon, polyaspartamide, metal oxides; porous silicates, metal organic frameworks and chitosan for CO_2 capture [151]. However, CO_2 capture by adsorption using activated carbon fibers and a carbon fiber component is regarded as an efficient approach when used in power plants [152]. Adsorption technology is attracting increasing attention due to its characteristics, which include minimum energy requirements, easy maintenance, simple operation and flexibility [153]. Amongst the adsorption processes reported in literature, temperature swing adsorption (TSA) is an advantageous process because it is inexpensive and uses less thermal energy. Therefore, it can reduce the operating costs if it is incorporated into coal-fired plants [154]. However, it requires longer cooling and heating times for CO_2 capture [155]. Meanwhile, vacuum swing adsorption (VSA) is more economically viable than pressure swing adsorption (PSA) in post-combustion for CO_2 capture [156]. Nevertheless, it has its own drawbacks, such as its sensitivity to feed gas temperature. More heat treatment might be needed to condition the flue gas before injecting it to the VSA plant; this affects the separation efficiency and process economics. PSA has been shown to be a promising technology in recent years because it can use a wide range of temperatures and pressures and requires minimum energy. Another advantage is that it requires low investment costs [157]. The adsorption technology also has its disadvantages, such as poor heat transfer, especially in packed beds, and slow kinetics, but the advantages of this technology far out-weigh its disadvantages [158]. There is potential in the implementation of this technology in the South African coal-fired power plants because of its ease of regeneration of the adsorbent using pressure modulation with reduced energy requirements.

4. The South African Power Sector

4.1. Power Generation in South Africa

South Africa has different options for power generation, which include nuclear energy, hydroelectric energy and wind energy [143]. South Africa is a main supplier of almost two-thirds of the electricity used in the African continent, and it falls among the top four least expensive electricity-producing nations globally. Over 90% of South Africa's electricity is generated from its coal-fired thermal power stations; 5% is generated from nuclear power plants, i.e., the Koeberg nuclear power station in Cape Town; and a further 5% of electricity is generated in hydroelectric power stations. However, there are only a few economic hydro sites that could be used for significant power generation in South Africa [147]. Approximately 52,017 MW of electricity are generated in South Africa, out of which 42,691 MW are generated from the combustion of fossil fuels, like coal. The remaining 9326 MW of electricity are generated from renewable, nuclear and hydro-electric stations, which are low CO_2-emitting power generation sources [16].

4.2. An Outlook for the South African Coal-Fired Power Plants

The major CO_2-emitting industries in South Africa are situated in the provinces of Gauteng, Mpumalanga and Free State. These regions form South Africa's coal mining sector, and most coal-fired powered plants are situated in these provinces, as well [17]. The electricity sector is predominantly dependent on coal energy, thereby making South Africa's coal-fired thermal power plants the largest CO_2 emitters in the country. Coal-fired power plants generate more than 90% of South Africa's electricity through the country's power parastatal, i.e., Electricity Supply Commission (ESKOM). Since 2008, new coal-fired power plants have been established in the coal-rich provinces of Mpumalanga and Limpopo. The Camden Power Station, which is located in Mpumalanga, generates about 156 megawatts of electricity, and it was established in 2008. The Grootveli Station was established in 2011 and has a production capacity of 1180 megawatts; it is also situated in Mpumalanga. Currently, two major coal-fired power plants are under construction, these include the Kusile and Medupi

power plants, which are expected to generate about 794–4764 megawatts of electricity supply in 2015–2020 [18].

The utilization of coal energy is expected to continue for the next decades because the country has enormous coal reserves, and this source of energy is inexpensive compared to other hydrocarbon fuels [19,20]. The country's power utility, Electricity Supply Commission (ESKOM) is listed amongst the highest CO_2-emitting companies in the world due to its use of pulverized coal combustion plants for power generation [21]. In 2010, South African coal-fired thermal power plants were among the highest CO_2 emitters in the world, as depicted in Table 1, i.e., South Africa was ranked ninth and generated 218 million tons of CO_2, with a total energy production of 215,000 GWh, out of which 93.4% was derived from coal. Therefore, mitigation strategies are highly emphasized by the South African government as a result of its heavy reliance on coal for electricity generation [21]. Consequently, the implementation of CCS technology is mandatory in South Africa's coal-intensive energy-grid in order to address the challenges of carbon emissions.

Table 1. World's largest CO_2 emitting coal-fired power plants by country.

Rank	Country	CO_2 Emitted (Megatons)	Energy Produced (GWh)	Fossil Fuel Power (%)	Reference
1	China	3120	3,620,000	82.5	[22]
2	USA	2820	4,190,000	68.8	[23]
3	India	638	719,000	76.3	[24]
4	Russia	478	896,000	63.4	[25]
5	Germany	429	636,000	62.1	[26]
6	Japan	414	1,030,000	33.2	[27]
7	U.K.	227	370,000	71.4	[28]
8	Australia	224	228,000	90.1	[29]
9	South Africa	218	215,000	93.4	[30]
10	South Korea	192	392,000	44.3	[31]

5. The Potential of CO_2 Capture and Storage in South Africa

South Africa is amongst the fast developing nations in the world and has a power sector that is mostly dependent on coal, i.e., the country generates up to 224 million tons of coal per annum. Owing to the country's strong commitment to sustainable energy development, it is necessary to understand the need for climate change mitigation options in the country's economic, social and environmental dimensions. With South Africa's high dependence on coal energy and the presence of streams of pure carbon dioxide in its coal-fired power plants, the application of CCS systems will be an attractive option to curtail the unfettered release of CO_2 into the atmosphere by the South African power sector [32]. The country's climate policy is deeply rooted in a strong commitment to a multilateral process under the Kyoto Protocol and the United Nation's Framework Convention on Climate Change (UNFCCC). South Africa is also a signatory to both the Kyoto Protocol and the United Nation's Framework on Climate Change; the country is committed to introducing measures to mitigate climate change, albeit it does not have quantifiable emission reduction targets under the Kyoto Protocol. Therefore, the country can benefit immensely by switching to a clean and sustainable energy development path through the CCS approach [33]. It can offer an environmentally-benign alternative in the utilization of coal energy in coal-fired power plants. Coal can still be used to fuel the power plants and yet reduce the emission of greenhouse gases like CO_2, instead of the so-called "business-as-usual" approach in which it is released into the atmosphere.

The theoretical maximum amount of capturable CO_2 in South Africa is approximately 64% of all anthropogenic CO_2 released [34–36]. Table 2 presents a breakdown of CO_2 contributing sources in South Africa and the amounts of CO_2 that are likely and unlikely to be captured if CCS technology were employed. It can be observed from Figure 2 that a higher percentage of CO_2 emitted in South Africa is capturable, and the majority of CO_2 emissions are generated by the power sector. Therefore, CCS technology would play a pivotal role in curbing the environmental pollution and health hazards caused by anthropogenic greenhouse gases, such as CO_2. A report from Engelbrecht et al. [35] indicated

that CCS systems can significantly reduce South Africa's CO_2 emissions if they are incorporated in coal-fired electricity-generating power plants [37]. The realization of CCS has been hampered by economic constraints, and its implementation has been discouraged in most developing countries due to high costs. Other barriers include lack of a framework, legislation and regulation from governments. Nonetheless, South Africa is a fast developing nation with sound economic policies that can fully implement CCS technology in these power plants, which is the country's major CO_2 emitter [14]. Furthermore, the implementation of CCS is economically feasible in South Africa, because it will primarily focus on coal-fired power plants, which will be less expensive than incorporating it in all sectors. South Africa can acquire skills from countries where the CCS technology is already functional and from sources like the European Directive on the Geological Storage of Carbon Dioxide (CCS Directive 2009/31/EC), which focuses on the geological storage of CO_2.

Table 2. Sources of CO_2 emissions in South Africa [35–37].

Source of Likely Capturable CO_2	Amount of CO_2 (Mt/a)	Source 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%		

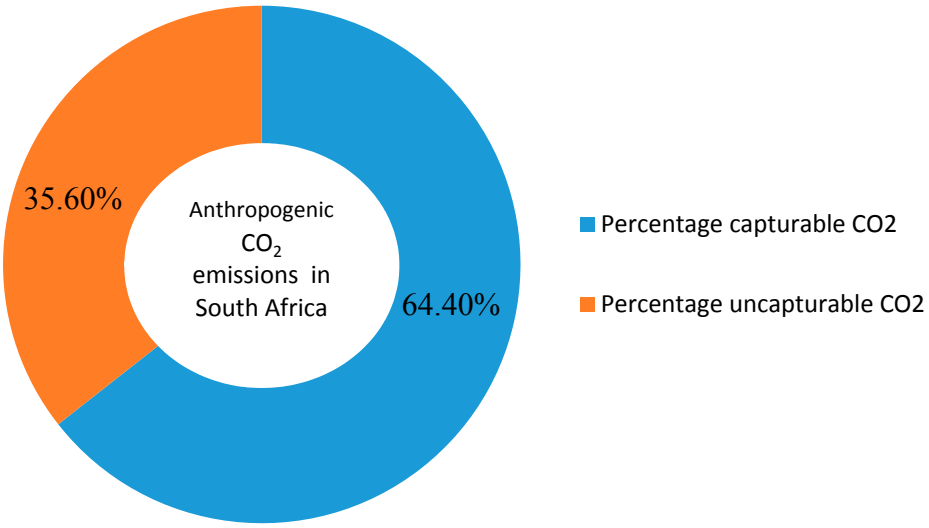


Figure 2. Percentage of capturable and uncapturable CO_2 in South Africa.

6. Geological Storage of CO_2

When CO_2 is successfully captured from these coal-fired power plants, it can be stored in natural areas, like geological formations, where it is trapped below impermeable rocks and retained in pore spaces after being dissolved by underground water [159,160]. This method of storing CO_2 has a long residence time. It can also be stored in geological formations, such as unused deep saline aquifers. According to literature reports, the geological storage of CO_2 is currently considered as the most viable option for storing captured CO_2 in large quantities [161,162]. Geological storage formations can store up to 10 million tons of CO_2 for a long period of time [163]. However, good geological sites for CO_2 storage must have: (i) appropriate thickness and porosity; (ii) the reservoir rock must be permeable and (iii) the cap-rock must be in a stable geological environment, as well as having a good sealing capability. Depleted or almost depleted oil and gas reservoirs, saline aquifers and un-mineable coal beds are the three major geological formations commonly considered for CO_2 storage [164]. Storing

CO_2 in deep oceans is another option for CO_2 storage; however, it poses environmental concerns, such as eutrophication and ocean acidification. Captured CO_2 could be stored in oceans by releasing it into deep ocean waters of a minimum depth of 1000 m below sea level. This form of CO_2 storage is feasible because cold-deep sea waters are unsaturated with CO_2 and subsequently have a significant potential of dissolving it. This is based on the principle that CO_2 becomes super critical below certain depths with a liquid-like density; and also, it is less buoyant than water [165]. However, as stated earlier, the major disadvantages of this option are the environmental challenges attributed to it.

South Africa has more geological formations than deep waters; therefore, the suitable option of storing the captured CO_2 from coal-fired power plants is by using geological formations, like deep saline aquifers at 700–1000 m below ground level. Carbon dioxide is soluble in water; there are natural exchanges of CO_2 between the atmosphere and waters at the ocean surface that occur until equilibrium is reached. If the atmospheric concentration of CO_2 increases, the ocean gradually takes up additional CO_2. In this way, the oceans have absorbed about 500 Gt CO_2 of the total 1300 Gt CO_2 of anthropogenic emissions released to the atmosphere over the past 200 years [166]. As a result of the increased atmospheric CO_2 concentrations from human activities relative to pre-industrial levels, the oceans are currently absorbing CO_2 at a rate of 7 Gt CO_2 per year. Most of this carbon dioxide now resides in the upper ocean and thus far, has resulted in a decrease in pH of about 0.1 at the ocean surface because of the acidic nature of CO_2 in water. To date, there has been virtually no change in pH in the deep ocean. Models predict that over the next several centuries, the oceans will eventually take up most of the CO_2 released to the atmosphere as CO_2 is dissolved at the ocean surface and subsequently mixed with deep ocean waters [167]. South Africa has various locations with great potential for CO_2 storage. For instance, the Karoo basin, which covers the Eastern Cape, Northern Cape, Free State, KwaZulu-Natal and the Mpumalanga provinces of South Africa, are very promising geological storage sites for the captured CO_2. The orange basin of Western South Africa around Durban and Zululand is another storage site available for the captured CO_2 from these power plants.

7. An Overview of CO_2 Capture Using Solid Adsorbents

CO_2 emissions from coal-fired power plants can be captured using solid adsorbents. Even though it is less mature than the absorption method, it is inexpensive, has minimum energy requirements and uses non-corrosive materials. Adsorption of CO_2 can be achieved by using various solid support systems, such as activated carbon, zeolites, carbon molecular sieves and polymeric adsorbents like amine-grafted polyaspartamide [168]. According to Chaffee et al. [165], physical adsorption of CO_2 using solid adsorbents require less energy as compared to other CO_2 capture systems. Physical adsorption of CO_2 requires about 0.09 KWh/kg CO_2 with equal pressure in the feed and product streams, which is by far smaller than the chemical adsorption, which requires about 0.34 KWh/kg CO_2. Yang et al. [166] conducted a study on modeling the physical adsorption of CO_2 using solid physical adsorbents and investigated CO_2 capture via the pressure swing adsorption methods using activated carbon, zeolite13X, and concluded that the adsorption technology is less expensive and less energy intensive for capturing CO_2. Similar findings were also confirmed by Othman et al. [167] when using molecular sieves and activated carbon materials. Rivas et al. [168] indicated that solid adsorbents are more efficient than liquid systems. For example, solid adsorbents exhibit better performance at partial pressures greater than 50 KPa of CO_2 [169–172]. However, liquid absorbents stabilize when coupled to chemical absorbents. Since the adsorption of gases is favored by higher pressures and lower temperatures, CO_2 capture from these power plants need to be carried out at high pressures; therefore, the adsorption technology will be ideal for effective CO_2 capture.

Physical adsorbents have also been proven to capture CO_2; they have a high affinity for CO_2. However, the purity of the gas decreases during the downstream process [173]. It was indicated that activated carbon and polymer-based adsorbents are the best type of physical adsorbents to be used for CO_2 capture. They produce about a 75%–80% pure CO_2 stream at a recovery of 90% [174]. Adsorption systems do not use high energy, and the recovery is far less than the chemical absorption methods [175].

Furthermore, polymer adsorption systems have been shown to bind CO_2. A study conducted by Diaf and Beckman [176] assessed the effects of polymers on CO_2 capture using primary, secondary and tertiary amine-based polymers, concluded that CO_2 binds strongly on basic amines and proposed ethylene diamine (EDA) as the most efficient amine compound for polymer system. Similar findings were also confirmed by Seckin et al. [177]; the authors used 1, 4, 5, 6-tetrahydropyrimidine polymer compound to capture CO_2 and concluded that this method was more feasible compared to other CO_2 capture methods. The effectiveness of CO_2 binding was due to the 1:1 nature of amidine groups in the 1, 4, 5, 6-tetrahydropyrimidine [174]. These findings could pave the way for the use of carbon dioxide capture technologies via amidine systems [175]. Recently, a novel polymer-based adsorbent "polyaspartamide" from polysuccinimide was identified as a promising adsorbent for CO_2 capture because of its ability to selectively adsorb gases; this is due to its molecular sieving characteristics [176]. The adsorbent was suggested in this study in order to address the limitations of conventional wet solvent processes for CO_2 capture at the pilot scale, such as high costs, high energy requirements and the generation of large quantities of water and sludge from the process [177]. Thus, the application of adsorption technology for CO_2 capture using amine-grafted polymer-based adsorbents is highly encouraged because it is a dry process and has fewer challenges as compared to the conventional process, which uses solvents for CO_2 capture.

8. Challenges Facing CO_2 Capture and Storage in South Africa

8.1. Economic Challenges

The implementation of CCS technology has been hindered mainly by financial constraints. The prices of incorporating CCS in power systems ranges between 30% and 70% depending on the method of CO_2 capture used [178,179]. Maver [180] showed that the challenges facing the implementation of CCS globally centers on economic, social and legal barriers; economic barriers in the sense that CCS is expensive and cannot be implemented by most developing countries. Nonetheless, South Africa is amongst the fast developing nations that have good economic frameworks and policies for successful implementation of CCS in its coal-fired power plants. There has also been some skepticism with regards to the deployment of CCS technology in South Africa; it has been debated that its implementation will threaten the country's efforts of developing renewable and sustainable energy resources because they also require huge financial incentives from the government [180]. Nevertheless, the CO_2 generated from the country's coal-fired thermal power plants is causing many challenges associated with environmental pollution and health hazards. It is essential to establish regulatory frameworks that will oversee this technology in South Africa [100]. Moreover, some of the economic barriers could be overcome by creating CCS financing mechanisms, whereby CO_2-emitting industries, e.g., Electricity Supply Commission (ESKOM) could contribute towards its financial development. A collaborative effort between various stakeholders can also accelerate its implementation [181].

8.2. Environmental Challenges

There are many environmental concerns associated with CCS; these include contamination of groundwater as a result of CO_2 leakage and the occurrence of earthquakes that might be caused by the sequestrated CO_2 due to pressure build-up [182]. The sequestrated CO_2 might be leaked into the atmosphere if it is stored in underground rocks and therefore escalates the problems of climate change. In addition, leakage could negatively affect soil quality; trees and other vegetation if stored underground [183]. In South Africa, this challenge could be surmounted because apart from storing the captured CO_2 in underground rocks, it can also be stored in the available basins listed in the previous chapters in this study. South Africa has abundant geological formations and un-mineable coal fields where captured CO_2 can be stored without infringing on environmental safety [184].

8.3. Social Challenges

The implementation of CCS may invigorate public debate because this technology is relatively new in South Africa and thus requires extensive research. Its long-term effects on the environment and people are not yet fully known. However, public awareness is essential in order to highlight its advantages, such as mitigation of CO_2 emissions and environmental degradation. This might in turn stimulate the interests of various stakeholders, which might contribute towards its implementation in South Africa [185]. South Africa through the South African Center for Carbon Capture and Storage (SACCCS) is creating public awareness on the need to curtail the indiscriminate emission of CO_2 in this region.

9. Conclusions and Recommendations

South Africa is a fast-developing nation with an energy economy that is highly dependent on coal, and it is apparent that the country has the potential for the implementation of CCS in the power sector. The potential for CO_2 capture lies in the major emitting sources, such as the electricity-generating coal-fired power plants, which are a major emitting source, as pointed out in this study. The establishment of the South African Center for Carbon Capture and Storage (SACCCS) illustrates the potential of the implementation of this technology in South Africa's power sector. There are various barriers facing the implementation of CCS globally. Nonetheless, it can be inferred that South Africa is a country with a strong commitment to sustainable and renewable energy and also a signatory to the Kyoto Protocol, as highlighted earlier in this review. This nation is working towards curtailing its carbon footprint by shifting its focus to major sources of CO_2 emission, such as the country's coal-fired thermal power plants. More so, it has included CCS policies into its legislation and has mandated SACCCS to oversee its implementation. This clearly brings to light that there is a huge potential of implementing CCS in the country's coal-fired thermal power plants. Thus, this review presented the potential of CCS technology in South African coal-fired power plants. The pressing challenges related to CO_2 emissions necessitate the search for clean and sustainable energy technologies, such as CCS in South Africa. The potential for CO_2 capture lies in the major emitting sources, which are the electricity-generating coal-fired power plants. The most suitable CO_2 capture route for the South African coal-fired power plants is post-combustion CO_2 capture, because it allows for easy retrofitting of capture devices in the existing coal-fired power plants. Adsorption technology using solid polymer-based adsorbents will be ideal and more economically viable for CO_2 capture in the South African coal-fired power plants.

The following recommendations are proposed for the implementation of CCS in South Africa's coal-fired power plants:

- The implementation of CCS has been stagnant in South African coal-fired power plants due to financial barriers, the lack of frameworks and the lack of technical expertise. Nonetheless, this challenge can be overcome by using solid inexpensive composite adsorbents, which have been shown in recent years to be economically viable, towards the improvement of CCS processes.
- Chemical absorbents, such as monoethanolamine, are extensively used in CO_2 capture. However, they have some limitations in terms of solvent capacity; it is therefore recommended that if the absorption technology must be used in post-combustion CO_2 capture from these South African power plants, a chemical absorbent with higher loading capacity, such as amine 2-amino-2-methyl-1-propanol (AMP) should be employed. Alternatively, the monoethanolamine can be coupled with activators, such as piperazine (PZ), to improve its efficiency, but if the adsorbents will be used as suggested by this study, these adsorbents should be impregnated with amine-rich materials, such as chitosan and polysuccinimide, because they increase the adsorbent's affinity for CO_2. Possible solid sorbents that could be used for CO_2 capture in the South African power plants include carbon nanotubes with chitosan impregnation, amine-grafted polyaspartamide, Sodalite-Zeolite Metal Organic Framework/chitosan composite materials, etc.

- Given the fact that the post-combustion CO_2 capture technology is highly embraced, its overall system performance with regards to South Africa's coal-fired power plants should be assessed by using pilot-plant experimental results from these power plants, and these results should be validated for their accuracy.

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Review

Biofuel Development Initiatives in Sub-Saharan Africa: Opportunities and Challenges

Patrick T. Sekoai * and Kelvin O. Yoro

Sustainable Energy & Environment Research Unit, School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Private Bag 3, Wits, Johannesburg 2050, South Africa; 1230119@students.wits.ac.za

* Correspondence: patricksekoai@gmail.com or 679314@students.wits.ac.za; Tel.: +27-84-807-3783; Fax: +27-11-717-7591

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Abstract: In recent years, biofuels have emerged as a suitable alternative to hydrocarbon fuel due to their foreseen potential of being a future energy resource. Biofuel development initiatives have been successfully implemented in countries like Brazil, United States of America, European Union, Canada, Australia, and Japan. However, such programmes have been stagnant in Africa due to various constraints, such as financial barriers, technical expertise, land availability, and government policies. Nonetheless, some countries within the continent have realized the potential of biofuels and have started to introduce similar programmes and initiatives for their development. These include the bioethanol production initiatives and the plantation of jatropha oil seeds in most Sub-Saharan African countries for biodiesel production. Therefore, this paper examines the biofuel development initiatives that have been implemented in several countries across Sub-Saharan Africa over the past few years. It also discusses the opportunities and challenges of having biofuel industries in the continent. Finally, it proposes some recommendations that could be applied to accelerate their development in these Sub-Saharan African countries.

Keywords: biofuels; feedstocks; Sub-Saharan Africa

1. Introduction

Africa is experiencing unprecedented and sustained growth. Currently, the continent has an estimated population of about 1.2 billion people. It is envisaged to have a population of about 2.5 billion people in 2050, which is double the current population [1]. According to a study conducted by the International Energy Agency in 2010, Africa had an estimated population of one billion and about 470 million people, representing 47% (Figure 1), had no access to electricity and were living without clean water facilities. Industrialization and population growth have been highlighted as major drivers affecting energy demands in most developing countries. However in African countries, energy demands will continue to intensify, mainly because of population growth. As a consequence, the population is projected to be 1.6 billion in 2030. This implies that the percentage of rural inhabitants without access to electricity is expected to reach 37%, corresponding to 592 million people, whereas 44% (704 million people) of urban dwellers will have access to electricity, as shown in Figure 1 [2].

Africa's economy is also growing at an average rate of 4% per year. A report from the International Renewable Energy Agency showed that six of the world's ten fastest growing economies over the past decade were in Africa. Thus, in order to maintain this growth as a continent, it was highlighted that the continent's gross domestic product (GDP) needs to increase three-fold by 2030 and seven-fold by 2050 [2]. However, sustaining such economic growth will only be possible if the continent has a thriving energy sector. The major drawback is that many countries within the continent are net oil

importers and have unstable economy *i.e.*, forty-two countries are net oil importers with the exceptions of Libya, Nigeria, Algeria, Egypt, and Angola [2].

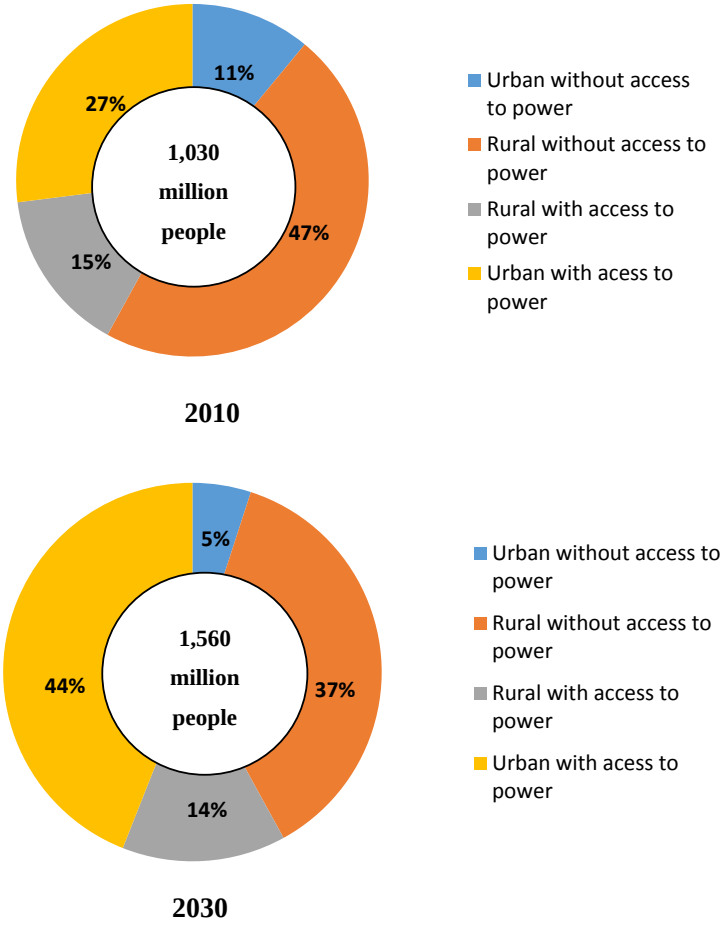


Figure 1. Shows the rural and urban electricity access for people living in Africa for the year 2010 and 2030 [1].

The unstable oil prices have also caused a huge financial burden on Sub-Saharan African oil importing countries, such as Benin, Burkina Faso, Cape Verde, Chad, Comoros, Eritrea, Gambia, Guinea, Liberia, Mauritania, Senegal, Seychelles, Sierra Leone, Somalia, Sudan, and Togo [3]. The price of oil is predicted to be nearly double in these countries than in oil producing markets. Furthermore, the demand for transport fuels is expected to grow by more than 5% year in these Sub-Saharan African countries during the period of 2005–2020 [4]. Other social challenges, such as political unrest, have resulted in severe damage to power facilities in Liberia, Somalia, Sierra Leone, the Central African Republic, and the Democratic Republic of Congo. Similarly, political conflict and economic downturn have negatively affected the power infrastructure in Zimbabwe [4]. Other countries, such as South Africa, are experiencing power outage due to rapid industrial growth. Another drawback is that they are relying on old power facilities that regularly require maintenance [5].

Therefore, these findings present a sense of urgency for the development of alternative energy fuels that will offer these Sub-Saharan African countries the prospect of self-sustainability with potential socio-economical benefits. Moreover, development of alternative energy fuels will have several advantages, such as alleviating the region's dependence on fossil-based fuels, cost-effective energy resources could be selected, more people can have access to electricity, and it could be cheaper to expand these technologies [6]. Biofuels are seen as a potential energy contributor in the next few decades and, thus, many countries are advocating policies that encourage their production and

consumption. Biofuels are considered a favourable alternative source of energy because (i) they are produced from sustainable energy crops; (ii) they can play a pivotal role in strengthening Africa's energy security; and (iii) improve infrastructural development programmes within the continent. This paper examines the biofuels development initiatives that have been carried out in some Sub-Saharan African countries. It discusses the opportunities and challenges of biofuel sector in Sub-Saharan African countries. Finally, it proposes some solutions that can be applied to boost their production.

2. Driving Forces behind the Intensification of Biofuels

The dwindling fossil fuels coupled with environmental degradation have triggered a worldwide interest in the establishment of an environmentally benign, carbon neutral and sustainable form of energy. Biofuels are considered a favourable alternative source of energy because they are produced from sustainable energy crops [7]. In industrialized countries, where greenhouse gas emission is a major challenge, the biofuel sector has been intensified to mitigate this problem. Thus, the worldwide production of biofuels has been increasing significantly over the past few years, from 20 billion litres in 2001 to more than 110 billion litres in 2011 [8]. During this period, the production of bioethanol and biodiesel increased exponentially. According to the US Environmental Protection Agency in 2010, it is expected that the production of biofuels will reach 222 billion litres by 2021 with bioethanol and biodiesel consisting of 81% and 19%, respectively, of this value [9]. It is important to note that a huge percentage of biofuels produced globally are generated from highly industrialized nations, such as the United States of America, Brazil, European Union, Australia, and Japan, in efforts to reduce their carbon footprints. However, in impoverished and underdeveloped regions, like Africa, biofuels are seen as a catalyst for infrastructural development projects, reducing high international oil prices, boosting the continent's energy sector, and the creation of employment opportunities. These are explained in Section 3.

3. Opportunities for Biofuels in Sub-Saharan Africa

The growing global interest in biofuels has prompted many African countries to start harnessing this form of energy. In the next two decades, it is envisaged that the biofuel sector will be a thriving one in most African countries, and will significantly contribute to the continent's infrastructural development programmes and economies. During this period, most countries are expected to formulate biofuel development policies that will regulate this sector [10].

In addition, the development of the biofuel sector presents many opportunities for poverty stricken nations in Africa. It has the long-term potential of boosting the energy sector of oil-importing countries. It can also boost the agricultural sector and could improve local infrastructures and rural development. For instance, farmers can grow specific crops that are used for biofuel production, and then receive incentives from local biofuel industries. Organic residues are also well suited for biofuels because they are easily available, inexpensive, and are considered as waste materials. Thus, the establishment of a biofuel sector will benefit the continent enormously, and this is elaborated below:

- Establishment of biofuel industries will assist rural communities to use the fuel for household electrification, powering farming machinery, and transportation.
- Development of biofuel initiatives will stabilise the continent's energy supply and diversify its fuel options and reduce the burden on oil importing countries.
- Some industrialised countries do not occupy enough land for cultivation of biofuel feedstocks, therefore African farmers can benefit by supplying raw materials to these nations.
- Construction of biofuel industries will provide many employment opportunities to African people and boost the continent's economy.
- Industrialised countries, such as Egypt, Nigeria, and South Africa, are amongst the leading carbon emitters in the continent. Therefore, commercialisation of biofuels technologies will assist in the mitigation of carbon emissions.

4. Biofuels Initiatives in Sub-Saharan African Countries

4.1. Burkina Faso

Burkina Faso is amongst the countries that are deeply affected by the energy crisis [11]. In efforts to curb this problem, biofuel development projects have been booming over the past few years. For example, 70,000 trees of jatropha oil seeds were planted in 2009 and government of Burkina Faso has been collaborating with the European Union Biofuel Directive since 2003 to boost this sector in their country [12]. Thus, biofuel development projects such as the Fondation Fasobiocarburant (FFB) were established, and are financed by Dutch investors [13].

4.2. Ghana

In 2010, Ghana introduced a bioenergy policy, which was created to substitute the country's petroleum oil with 10% biofuels by 2020 and 20% by 2030, respectively [14]. The country introduced this policy with the intention to utilise the vast majority of biomass resources that are abundant in Ghana for the generation of transport fuels and electricity. Biomass resources, such as cassava, sugarcane, maize, and jatropha oil seeds, were identified as potential feedstocks for bioethanol and biodiesel production in Ghana [14].

4.3. Mali

There are a number of biofuel projects that are currently underway in Mali, one of which includes a local non-governmental organization (NGO) referred to as the Mali-Folke Center Nyetaa, which offers assistance to local farmers to grow jatropha oil seeds [10]. Communities living near the Mali-Folke Center are provided with electricity generated from power plants that uses jatropha oil seeds. The project has embarked on a 15-year electrification programme, which aims to generate 300 KW of electricity to more than 10,000 rural residents. It is expected that more than 100 hectares of jatropha plantation will be established and used as feedstock for the production plant [10]. This will boost the livelihood of these communities.

4.4. Malawi

In 2006, an eight million US dollar biodiesel-based production plant was launched in Malawi's capital city, Lilongwe [15]. The project was led by Dutch investors, and currently processes up to 250 tons of jatropha oil seeds per day to produce 5000 litres of biodiesel. Thousands of local farmers have benefited from this initiative and they have been contracted to plant ten million jatropha trees over a period of five years; these trees will serve as raw materials for the production plant [15]. Other biofuel initiatives include the bioethanol production plants in Dwangwa Estate, which produce 15–20 million litres of bioethanol from sugarcane molasses, and the Nchalo Plant, which has a production capacity of 12 million litres per annum [16]. These plants jointly blend 10% (v/v) of bioethanol with petrol [16].

4.5. Mozambique

Various biofuel production initiatives have also been implemented in Mozambique over the past few years. For example, the Ndzilo Production Plant has a capacity of two million litres of ethanol processed from cassava [17]. With regards to biodiesel production, jatropha oil seeds have been gaining an increasing attention in Mozambique due to their advantages, which include sustaining harsh dry conditions. Companies, such as Petromoc and SunBiofuels, have established biodiesel production factories over the past few years in order to boost the country's energy sector [17]. The Mozambican government has implemented the blending of 5%–10% (v/v) bioethanol with petrol [10].

4.6. Nigeria

There is a growing response with regards to the production of biofuels in Nigeria. Therefore, various biofuel and biodiesel production initiatives ranging from feasibility studies to refinery plant installation have been carried out [18,19]. Currently, five major commercial-scale ethanol distilleries produce up to 134 million litres of ethanol per annum in Nigeria (Ohimain, 2010). Biodiesel production projects that have been initiated include Biodiesel Nigeria Limited in Lagos State, Aura Bio-Corporation in Cross River State, and the Shashwat Jatropha in Kebbi State [18].

4.7. Senegal

Over the past few years, the Senegalese government has developed various biofuels development initiatives in order to improve the country's energy sector. This was achieved by collaborating with biofuel experts from countries such as Brazil and India. Through this initiative, several biofuel projects were carried out in Senegal, *i.e.*, the inclusion of the plantation of jatropha oil seeds, which were grown on four thousand hectares of land in the city of Touba [20]. Other feedstocks, such as castor oil and sunflower, were also assessed and cultivated on more than fifty thousand hectares of land in Kolda and Tambacounda [20].

4.8. South Africa

Biofuels are amongst the highest renewable energy contributors in South Africa, with an estimated contribution of 9%–14% [21]. In 2013, The Department of Energy in South Africa announced that it aims to begin a mandatory blending of petrol and diesel with biofuels (bioethanol and biodiesel) as of 1 October 2015, as the country moves towards strengthening its biofuel sector, thereby reducing its reliance on imported fuel [21]. The country also proposed a five-year pilot phase plan, which is aimed at achieving 2% biofuel in the country. Therefore, five companies have been granted licenses to generate bioethanol and biodiesel in South Africa. Analysis of potential feedstocks that can be used reveals that sorghum is suitable for bioethanol production, while soya beans are also potential feedstocks for biodiesel production [21]. However, maize has been excluded from these feedstocks because it is one of the country's most stable foods with an estimated annual production of 8 million tons, and this may affects the country's food security. In addition, South Africa is experiencing a very large influx of biomass generated from the agricultural, municipal, and industrial sectors. Thus, other potential biofuel options, such as biomethane, bioelectricity and biohydrogen production, would play a pivotal role in country's energy mix.

4.9. Tanzania

In Tanzania, a number of companies, NGOs, and small-scale farmers are implementing biofuel programmes in the country [22]. These initiatives are elaborated on below.

- Diligent Tanzania Ltd.—the company focuses on the production of jatropha oil and biodiesel, but offers some consultancy services to jatropha farmers.
- Kakute Ltd.—is a privately owned company, which was established in 1995. It focuses on training farmers with jatropha plantations, oil processing, and the ARI-Monduli (Alternative Resource Income for Monduli Women) project, where local women farmers are assisted in the production of jatropha oil seeds.
- MVIWATA—this is a Tanzanian farmer's organization that was initially comprised of approximately 2000 small-scale farmers, aiming at planting jatropha oil seeds.
- Kikuletwa Farm—this farm is owned by Peter Burland and previously produced aloe vera; however, in 2002, he saw a great deal of potential in jatropha oil seeds and started to plant large hectares of it on his land. He has since been contracted by various companies to produce jatropha oil seeds.
- Jatropha Products Tanzania Limited—this organization is tasked with promoting the production of jatropha in Tanzania and has been in existence for many years.

- Tanzanian Traditional Energy Development and Environment Organization—this is a Tanzanian NGO that assists rural small-scale farmers and has projects running concurrently in Dar es Salaam and the Monduli District. It supports farming related to jatropha oil seeds.

There are also other biofuel initiatives that are being conducted in Benin, Burkina Faso, Ivory Coast, Guinea, Kenya, Ethiopia, Niger, Sudan, Swaziland, Senegal, Togo, and Uganda. These are summarised in Table 1; it can be observed that molasses is a popular feedstock for bioethanol production in many African countries, while jatropha oil seeds are common for biodiesel production. Table 2 shows the oil yields extracted from different feedstocks; these oils are used in biodiesel synthesis. It can be noted that the oil yields vary significantly due to various contributing factors, such as nutritional composition of feedstocks, soil content, and climate conditions in which the energy crops are grown under [10].

Table 1. Biofuel production from agricultural waste in Sub-Saharan African countries [10].

Country	Feedstock	Biodiesel Yield (ML)	Bioethanol (ML)
Benin	Cassava	-	20
Burkina Faso	Sugarcane	-	20
Ivory Coast	Molasses	-	20
Ghana	Jatropha	50	-
Guinea	Cashew	-	10
Mali	Molasses	-	20
Malawi	Molasses	-	146
Kenya	Molasses	-	413
Ethiopia	Molasses	-	80
Niger	Jatropha	10	-
Nigeria	Sugarcane	-	70
Sudan	Molasses	-	408
Swaziland	Molasses	-	480
Senegal	Molasses	-	15
Tanzania	Molasses	-	254
Togo	Jatropha	10	-
Uganda	Molasses	-	119

ML: megalitres; -: data not available.

Table 2. Oil yields from various feedstocks across Africa [10,23].

Feedstock	Litres of Oil Per Hectare	Countries That Grow Feedstock
Palm oil	5950	Angola, DRC, Ghana, Nigeria, Tanzania
Soya beans	446	DRC, Ghana, Malawi, South Africa, Tanzania
Coconut	2689	Ghana, Mozambique, Nigeria, Senegal, Tanzania
Jatropha	1892	Benin, Tanzania, Malawi, Mozambique, Nigeria, Ghana
Sunflower	952	Angola, Botswana, DRC, Ghana, Malawi, Nigeria
Cotton seed	325	Angola, Ghana, Malawi, Mozambique, Tanzania, South Africa, Zambia, Zimbabwe
Avocado	2638	DRC, Ghana, Nigeria, Senegal, South Africa
Groundnuts	1059	Angola, DRC, Gambia, Ghana, Malawi, Mozambique, Senegal, Zambia, Zimbabwe
Cashew nut	176	Angola, Ghana, Mozambique, Nigeria, Tanzania
Castor beans	1413	Angola, DRC, Mozambique, South Africa

Biodiesel can be synthesized from various feedstocks, including edible and non-edible oils, as shown in Tables 2 and 3, respectively. However, the utilization of edible oils presents many challenges, *i.e.*, many African countries are experiencing a shortage of food supply. Therefore, non-edible oils

are ideal substrates because they do not impose a threat to food security and many can be cultivated under various climatic conditions. Furthermore, the increase in world population puts pressure on the global food supply, and, hence, biofuels experts are focusing on feedstocks that are considered waste materials and easily cultivable.

Table 3. Oil content from non-edible feedstocks.

Feedstock	Oil Content			References
	Seed (wt %)	Kernel (wt %)		
Jatropha	20–60	40–60		[24]
Karanja	25–50	30–50	-	[24]
Neem	20–30	25–45	-	[24]
Mahua	35–50	50	-	[24]
Kusum	10.65	-	-	[25]
Castor	45–50	-	-	[24]
Linseed	35–45	-	-	[24]
Sea mango	54	6.4	-	[24]
Tobacco	17–25	17	-	[26]
Mexican prickly poppy	22–36	-	-	[26]
Rubber tree	40–60	40–50	-	[24]
Persian lilac	10	-	-	[26]
Jojoba	45–55	-	-	[26]
Yellow oleander	8.41	-	67	[26]
Moringa	33–41	-	2.9	[26]
Field pennycres	20–36	-	-	[27]

-: data not available.

5. Feedstocks Used for Biofuel Production

5.1. Bioethanol Production

Bioethanol can be synthesised using various organic materials that are comprised of fermentable sugars, such cellulose and hemicellulose [28]. Research over the past few years has been focusing on the utilisation of agricultural waste in order to make this process economically feasible. It was estimated that approximately 491 billion litres of bioethanol can be produced from agricultural waste materials, such as rice straw, wheat straw, corn straw, grasses, sawdust, sugarcane molasses, and woody chips [29]. These feedstocks are advantageous for bioethanol production because they are highly abundant, inexpensive, and renewable. Moreover, bioethanol can be produced from edible feedstocks, such as barley, sugarcane, sorghum, and cassava; however, their usage is discouraged due to the food shortages facing many impoverished countries.

5.2. Biodiesel Production

Biodiesel can be produced from oils and fats that are extracted from animal fats, and non-edible oleaginous plants, such as jatropha oil seeds, and other non-edible plants, as shown in Table 3 [30].

6. Social Concerns Related to Biofuels in Sub-Saharan Africa

6.1. Land and Food Security

Land is the biggest asset that forms the foundation of all human life. Therefore, more than 60% of the people in Angola, Mozambique, Namibia, Tanzania and Zimbabwe reside in rural areas, whereas more than 70% live in rural areas in countries like Lesotho, Madagascar and Malawi [31]. There has been some scepticism with regards to the usage of land for biofuel production in Africa because a vast majority of the countries are primarily dependent on agriculture as a means of survival. Commercialisation of biofuels will require many hectares of land, and this might cause a major problem

for the livelihoods of people. For example, agricultural work is carried out by women organizations and small-scale farmers in most countries in West Africa. Therefore, if the arable land is used for cultivation of biofuel feedstocks, this will reduce their agricultural outputs and, thus, affect their basic living conditions [32].

In a meeting held in Rome in 1992, the World Food Summit defined food security as the ability of all people to access food that is needed for healthy living at all times [33]. Shortage of food has been identified as a major problem facing most countries in Africa, and was highlighted in the Millennium Development Goal (MDG) as one of its priorities [34]. Recent food security crises have also invigorated the debate of biofuel production potential in African countries, given the fact that most of them depend on local agriculture for sustenance. Land plays a crucial role in the livelihoods of Africans; therefore, food security and poverty alleviation will be achieved if the land is firstly prioritized to people's needs and is then catered to biofuel industries.

Nevertheless, countries with favourable climate conditions and land potential are at an advantage for the biofuel sector, and have the possibility of developing their agricultural regions [35]. Therefore, it is pivotal for governments in Africa to regulate the distribution of land in order to prevent the exploitation of people, especially impoverished small-scale farmers, by the biofuel markets.

6.2. Environmental Impact

From an environmental point of view, the production of biofuels may cause serious detrimental effects on the environment, such as the utilisation of large quantities of water, the utilisation of arable land that could have been used for crop farming, destruction of forests, destroying the ecosystem and biodiversity, and alteration of soil structure and fertility. Furthermore, many biofuel production feedstocks require high quality agricultural land, and use fertilisers, pesticides, and water to produce high biofuel yields [36]. Therefore, researchers have proposed various scientific methods to mitigate such problems. They have developed a useful tool that is used to determine the environmental impact of biofuels, *i.e.*, Life Cycle Analysis (LCA), which evaluates the consumption and impacts of a product throughout its life stages [30].

Several studies in the literature have used this method to evaluate the environmental impact of bioethanol production. For example, Blottnitz and Curran [35] compared bioethanol production with conventional fuels using LCA and the analysis concluded that, (i) it is more feasible to attain high bioethanol yields from feedstocks consisting of rich fermentable sugars located in tropical countries than those feedstocks which are cultivated in temperate regions; and (ii) these feedstocks must undergo hydrolysis followed by a fermentation process. Other studies used indicators to compare several feedstocks in relation to biofuel production yields [37]. One of the indicators is the replacement potential of fossil fuel (expressed in $GJ \cdot ha^{-1} \cdot year^{-1}$), and another indicator that is used is derived from the relation renewable/fossil energy (output/input) for biofuel feedstock. Pimentel and Patzek [36] showed unfavourable results for biodiesel production from sunflower and soybeans. This was due to low production yields and high energy input [38]. Table 4 shows the strengths, weaknesses, opportunities, and threats of biofuels in Sub-Saharan Africa.

Table 4. Strengths, weaknesses, opportunities, and threats of biofuels in Sub-Saharan Africa.

Strengths:	Reduction in imported petroleum oil
	Reducing the dependency on fossil fuels
	Carbon sequestration
	Reducing greenhouse gas emissions
	Energy security

Table 4. *Cont.*

Weaknesses:	High capital costs Low energy yields Requirements for large hectares of land Affects the ecological systems Ineffective governing policies
Opportunities:	Increased job opportunities Increased income for rural people Diverse fuel options Infrastructural development Increased electricity supply
Threats:	Reduction in the availability of land Affects the soil fertility Food insecurity, if edible feedstocks are used Some feedstocks requires high water content

7. Economic Evaluation of Biofuels in Sub-Saharan Africa

The economic factors involved in biofuel production include the capital costs, raw materials, plant capacity, maintenance costs, and process technology [39,40]. It has been shown in several studies of biofuel production that the cost of raw materials is considerably high, *i.e.*, it comprises 75%–80% of the total operating costs [41–44]. In the case of biodiesel production, the oils in vegetable seeds need to first be extracted, refined, then used in the transesterification process. Whereas the lignocellulosic agricultural materials used for bioethanol production must undergo a vigorous pretreatment process to ensure that the fermentable sugars are released. Other factors to consider include labour, storage, and transportation costs. A feedstock cost of US $0.539/L was estimated for biodiesel production when using refined soy oil [45]. Meanwhile, a cost of US $0.97/L was predicted for bioethanol production from sugarcane bagasse [46]. It has also been noted that the costs of biofuels vary from each region due to contributing factors, such as the type of feedstock used and production scale.

Currently, the cost of large-scale production of biofuels is high in industrialized nations. For instance, biofuel costs are considered to be three times higher than that of hydrocarbon fuels. On the contrary, in underdeveloped regions, such as Sub-Saharan Africa, the costs are very low due to low production-scales and non-existence of biofuel markets [47]. Large-scale production of biofuels in Sub-Saharan African countries will necessitate the development of novel technologies to ensure that this market is strengthened by improving the energy yields, and thus make it economically competitive to petroleum oil. This implies that various stakeholders need to be actively involved towards biofuel development initiatives in the continent [48–50].

8. Conclusions and the Way Forward

This paper examined the biofuel initiatives that have been implemented in Sub-Saharan Africa over the past few years. It also examined the opportunities and threats of implementing biofuel initiatives in this region. Biofuels could offer a great deal of relief to most oil-importing countries in Africa through the blending of imported hydrocarbon fuels with biofuels. However, many governments have been slow to introduce biofuel development initiatives in their countries due to several bottlenecks, such as lack of biofuel policies, lack of technical expertise, financial constrains, and food security and land issues. Nevertheless, with the growing global interest in biofuel programmes, Africa need to strategically position itself by assessing international developments in biofuel initiatives and acquire major skills (e.g. technical expertise, frameworks) which could be attained by collaborating with leading biofuel-producing nations through knowledge exchange and financial support. In addition, biofuel initiatives will serve as a catalyst for economic growth, infrastructure development, and social welfare in Africa. In order to ensure that biofuels technologies

are implemented in Africa, it is imperative for various governments within the continent to invest enormously in these technologies by:

- Implementing national biofuel regulatory policies and strategies that will boost their development and accelerate their large-scale production.
- Investing in biofuel infrastructure development, such as production, processing, storage, and transportation.
- Investing in biofuel resources and technical expertise.
- Collaborating with various stakeholders, such as industries, farmers, academics, and NGOs.
- More research and development programmes should be carried out in order to accelerate development.
- More research and development is needed to advance from first generation biofuels (bioethanol and biodiesel) to commercial-scale production of second (biomethane and biohydrogen) and third generation (algae) biofuels in order to strengthen the biofuel market.
- Countries like Brazil are well suited for biofuels because they have outstanding climatologic conditions and have seasonal rainfall that favours the cultivation of biofuel feedstocks. Therefore, it is mandatory for each country to assess their own resources, *i.e.*, land availability, water resources, climate conditions, and costs.
- Even though the biofuel sector has a great deal of potential in Africa, proper and systematic laws are needed to govern this sector to ensure that it does not compromise the livelihood of people and the environment. Thus, biofuel feedstocks should be cultivated on land that is not used for crop farming. Secondly, a proper environmental assessment is necessary to ensure that each country's biodiversity is not affected, *i.e.*, countries are encouraged to use indigenous biofuel feedstocks instead of alien plants in order to prevent potential threats to ecological systems.
- The impact on food security should be thoroughly assessed so that the biofuel sector uses crops that are not required for human consumption. For example, more than 95% of biodiesel produced globally is currently derived from edible oils [51]. The use of edible feedstocks imposes a large challenge on food supply, as mentioned earlier. Focus should be directed towards non-edible resources since they do not compete with human consumption and could be cultivated on barren land fields. In addition, the production of biodiesel from non-edible oils will offer several advantages, such as a reduction in production costs and mitigation of atmospheric carbon dioxide. Therefore, it is essential for governments to implement the plantation of non-edible oleaginous (e.g. jatropha oil seeds) to protect the livelihoods of people.
- Other alternative forms of energy, such as wind, solar, nuclear, and geothermal energy, should also be integrated into the energy mix in order to mitigate the pressing energy crisis facing the African continent. Sub-Saharan countries like South Africa have intensified their renewable energy production by diversifying their options. Over the past few years, the Department of Energy of South Africa has initiated a programme that focuses on the implementation of solar energy. For instance, approximately 400,000 homes are installed with solar water heaters every year [52]. The use of solar water heaters is driven by the socio-economical needs for energy security, environmental sustainability, and reducing the usage of electricity. Moreover, a five-year, long-term plan of installing solar water heaters across the country by 2020 has been proposed by the South African government. South Africa's power parastatal Eskom installed a 25-kW solar panel in 2012 as part of the initiatives from the South African government to assess this technology. Other renewable energy projects include the installation of windmills. In 2014, South Africa launched one of its biggest wind farms in Africa, *i.e.*, the Jeffrey's Bay Wind Farm, located between the farms of Jeffrey Bay and Humansdorp in Eastern Cape, which was built by the British-based company Globleleq. The farm comprises 60 (80-metre high) wind turbines, which spread over 3700 hectares, and can produce up to 138 megawatts of electricity [53].

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Modelling and Experimental Study of the CO_2 Adsorption Behaviour of Polyaspartamide as an Adsorbent during Post-Combustion CO_2 Capture

Kelvin O. Yoro, Muofhe Singo, Jean L. Mulopo, Michael O. Daramola*

School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Private Bag X3, Wits 2050, Johannesburg, South Africa.

Abstract

Adsorption technology due to its potentially low energy consumption, simple operation and flexibility in design to meet different demands is fast becoming popular and is now widely considered in the area of CO_2 capture. Adsorbents play a vital role in any adsorption technology. Therefore, the behavior of adsorbents under different conditions during an adsorption process needs to be investigated. In this study, the behavior of polyaspartamide as an adsorbent during post-combustion CO_2 capture was investigated using kinetic and non-kinetic models. Bohart-Adams and Thomas models were the non-kinetic models explored to ascertain whether external mass transfer dominated the overall system kinetics during the CO_2 adsorption onto polyaspartamide. The kinetics of adsorption of polyaspartamide was studied using Lagergen's

* Corresponding author. Tel.: +27 11 717 7536.

E-mail address: michael.daramola@wits.ac.za

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pseudo 1st order, Lagergen's pseudo 2nd order and the Avrami kinetic models in order to understand whether the adsorption process was a physical, chemical or physiochemical process. The experimental validation of the model prediction was carried out in a laboratory-sized packed bed adsorption column at an operating pressure of 2 bar; gas flow rate of 1.5-2.5 ml/s, and a temperature range of 303-333 K using 0.1 g of the adsorbent. The experimental breakthrough curve showed a superior fit with the Bohart-Adams model. For the kinetic study, Avrami kinetic model displayed a better fit with kinetic data at all temperatures studied. The non-kinetic model revealed that external mass transfer governed the adsorption of CO_2 onto polyaspartamide while the kinetic study revealed that the mechanism of adsorption of CO_2 onto polyaspartamide was more of physical than chemical (physiochemical).

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Keywords: Adsorbents; Adsorption; Breakthrough curves; CO_2 capture; Polyaspartamide;

1. Introduction

The interest in CO_2 capture is rising continuously around the globe. Carbon capture and storage (CCS) is a promising technology for mitigating climate change and meeting CO_2 emission reduction targets [1]. Anthropogenic CO_2 emitted into the atmosphere must be reduced in order to mitigate the unfettered release of greenhouse gases into the atmosphere [2, 3]. The Capture of CO_2 from flue gas emitted from power plants via post combustion capture is very useful in addressing the problem of its emission into the atmosphere. Post-combustion CO_2 capture via the adsorption technology ensures that the adsorbent is in direct contact with the CO_2 gas in an adsorption column. Mathematical models describing the behavior of the adsorbent during the post-combustion CO_2 capture is very essential in designing, optimizing and scaling-up of the CO_2 capture process[3, 4]. Furthermore, thermodynamic and kinetic study play a role in understanding the performance of any adsorbent [4]. The solute uptake rate which determines the residence time required for completion of the adsorption process can also be established from the kinetic analysis. Several mathematical models have been developed to describe adsorption behavior of adsorbents during post-combustion CO_2 capture. Due to the complex nature of the mathematical model solutions, the use of accurate and simplified models have been explored to

reduce the computational time [5]. Mathematical modeling of adsorption processes have attracted a considerably high attention amongst researchers today because mathematical models are capable of estimating the breakthrough curve, adsorption kinetics and temperature profile for a certain adsorbent and adsorbate in all locations within the adsorption column [5-6]. The model, if experimentally verified can be used to study the effect of various process parameters such as pressure, temperature, flow rate and concentration on the adsorption behavior of an adsorbent. CO_2 capture using solid adsorbents involves a selective separation of CO_2 based on a gas–solid interaction [7]. The adsorbent in most adsorption processes is always in contact with the gas in a packed bed adsorption column [8]. An understanding of the behavior and performance of the adsorbent and also the dynamic behavior of the adsorption system is required for a rational process design, scale-up and optimization [9-11].

In recent times, several adsorbents have been synthesized and investigated for CO_2 capture using experimental and modeling approach [12-14]. Examples are synthetic zeolites, activated carbon, carbon molecular sieves, silica, metal oxides, chitosan, carbon nanotubes, Sodalite zeolite metal organic frameworks (Sod-ZMOFs) etc. Before designing an adsorption process, selecting an appropriate adsorbent with high working capacity as well as a strong desorption capability is key for post combustion CO_2 capture [9]. This simply means that adsorbents play a key role in any adsorption technology [15]. For instance, adsorbents determine the overall CO_2 capture performance in the vacuum swing adsorption (VSA) technology [16]. The key elements for a good adsorbent in CO_2 capture technology are; high selectivity of CO_2 , high adsorption capacity, rapid adsorption/desorption kinetics, stable adsorption capacity after repeated cycles and adequate mechanical strength of the particles [17]. Amine-modified polymer-based adsorbents have been developed recently [18]. Polyaspartamide has been studied as a potential adsorbent for post-combustion CO_2 capture [19]. Polyaspartamide (PAA) is an amine grafted polymer from polysuccinimide obtained when polysuccinimide reacts with Ethylene diamine (EDA). Polyaspartamide is considered as a potentially good adsorbent for post combustion CO_2 capture because of its large surface area, non-toxic nature, biodegradable nature and its good geometry [20]. The behavior and performance of polyaspartamide as an adsorbent is assessed in terms of various desired attributes, such as its equilibrium adsorption capacity, regeneration,

multi cycle durability, and adsorption/desorption kinetics. In this study, existing gas-solid kinetic and non-kinetic adsorption models will be used to assess the behavior of polyaspartamide during post combustion CO_2 capture using a balanced flue gas stream of 15% CO_2 and 85% N_2. This study focused on investigating the adsorption behavior of polyaspartamide as an adsorbent during post combustion CO_2 capture using mathematical modeling and experimental validation approach. Other properties to test for the performance of polyaspartamide during CO_2 capture such as adsorption kinetics was also studied using kinetic models.

Nomenclature

% E	Percentage Error
C	Final concentration of CO_2
CCS	carbon capture and storage
C_e	Concentration of CO_2 at equilibrium
C_o	Initial concentration of CO_2
EDA	Ethylene Diamine
K_A	Avrami constant (s^{-1})
K_f	Pseudo 1st order constant (S^{-1})
K_s	Pseudo 2nd order constant ($gmol^{-1}s^{-1}$)
N	Number of experimental runs
nA	Avrami exponent
PAA	Polyaspartamide
qe	Amount of CO_2 adsorbed at equilibrium ($mol\ g^{-1}$)
Q_{Exp}	Amount of CO_2 adsorbed from experiment ($mol\ g^{-1}$)
Q_{mod}	Amount of CO_2 adsorbged predicted by the model ($mol\ g^{-1}$)
q_t	Amount of CO_2 adsorbed at a particular time ($mol\ g^{-1}$)
t	Time (seconds)
VSA	Vacuum swing adsorption

2. Experimental Section

2.1 Materials

The adsorbent considered in this study is polyaspartamide. Detailed information about the synthesis and characterization of the adsorbent can be obtained elsewhere [10, 19]. As such, it will not be repeated in this study. The gas used was a balanced mixture of CO_2 and N_2 (15% CO_2, 85 % N_2) purchased from Afrox (pty) South Africa. The experiment was carried out in a laboratory-scale packed bed adsorption column. The experimental conditions for this study are summarized in Table 1.

Table 1. Experimental conditions for adsorption

Operating conditions	
Adsorption temperatures (K)	303 - 333
Adsorption total pressure (bar)	2
Inlet flow rates (ml/s)	1.5 – 2.0
Inlet gas concentration (vol. %)	15.0
Mass of adsorbent (g)	0.1

2.2 Method

0.1 g of polyaspartamide was fed into the packing in the adsorption column and degassed by passing in dry Nitrogen gas through the packed bed at an inlet flow rate of 1.5 ml/s and a temperature of 373 K for 1 hour to remove CO_2 that could be present within the adsorption column. Polyaspartamide was heated to 373 K within the adsorption column to remove moisture that could be present on the adsorbent and also improve its porosity. After the degassing and heating stage, the temperature of the adsorption bed was lowered to 303 K under N_2 flow. The flue gas mixture (15% CO_2, 85 % N_2) was fed to the packed bed adsorption column at a flow rate of 2.5 ml/s while by-passing the reactor in order to determine the inlet concentration of CO_2 from the gas analyzer (model: ABB-AO2020). The flue gas was then allowed to pass through the reactor containing the adsorbent. The gas flow rate was regulated using a mass flow controller while the CO_2 uptake onto the polyaspartamide material was monitored as a function of time from the CO_2 gas analyzer. The experiment was repeated at temperatures of 318 and 333 K and flow rates of 1.5 and 2.0 ml/s to determine the behavior of the adsorbent at higher temperatures and different flow rates. The experiment lasted for 1200 seconds until equilibrium was reached. A schematic process flow diagram for this experiment is depicted in Figure 1.

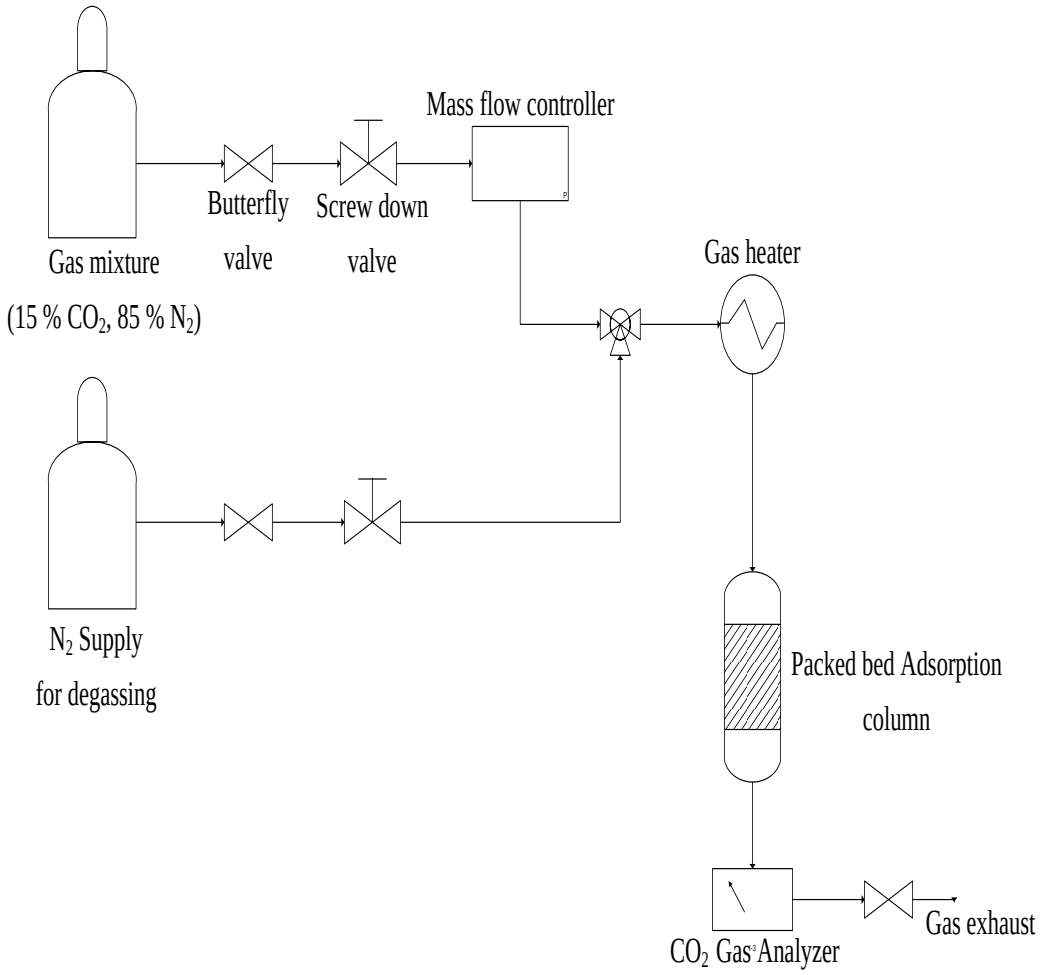


Figure 1. Experimental set up for CO_2 adsorption onto polyaspartamide material in a packed bed column.

3. Model description and Implementation

3.1 Model description

The models considered in this study were existing gas-solid adsorption models derived from the mass balance around an adsorption column. Assumptions for the models explored in this study are summarized in Table 2.

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Table 2. Models explored and the basic assumptions made

Models Studied	Assumptions
Bohart-Adams model	1. Rectangle or step isotherm is assumed for the model and adsorption bed is homogenous 2. Gradients occur only in the axial direction and they are negligible 3. At time t = 0, the bed is free of adsorbate (CO_2) 4. The model assumes that equilibrium is not instantaneous 5. Irreversible adsorption isotherm
Thomas Model	1. The axial and radial dispersion in the column is negligible 2. Constant separation factor 3. Adsorption is described by a pseudo-second order reaction rate principle and reduces to a Langmuir isotherm at equilibrium. 4. The column void fraction is constant 5. Constant temperature and pressure process conditions 6. Negligible external resistance during mass transfer process.
Lagergen's pseudo 1st order model	1. The rate of adsorption increases as the number of vacant site on the adsorbent increases 2. Local equilibrium is achieved instantaneously and the primary resistance is mass transfer resistance.
Lagergen's pseudo 2nd order model	1. The rate of adsorption is proportional to the square of the number of vacant sites
Avrami kinetic model	1. There are random nucleation sites across the reaction surface

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3.2 Model implementation

Experimental data were fit into the Bohart-Adams model, Thomas model, Lagergen Pseudo 1st and 2nd order models as well as the Avrami kinetic model, to describe the behavior of the adsorbent. Kinetic data significantly influence the residence time required for the completion of any adsorption process as well as the unit capital cost [21]. In this study, the kinetics of adsorption of polyaspartamide was investigated using the Lagergen's pseudo 1st order, 2nd order and Avrami kinetic models. The kinetic models used to describe the adsorption kinetics were validated using kinetic data obtained from the experiment conducted. Due to complexities associated with the description of model parameters, this study considered a common approach which involves fitting of the data obtained from experiments to a number of mathematical models. The model that fits best with the experimental data is always considered as the best model describing the behavior of the adsorbent [22]. Breakthrough curves in this study were obtained by plotting the normalized concentration of CO_2 (C/C_o) against time. The breakthrough curves were obtained at various temperatures and also different flow rates. The breakthrough curves in this study were described using the Bohart-Adams and the Thomas model [23, 24]. The model results were validated using the experimental data. Model parameters obtained from the solution in MATLAB R2014a are presented in Table 4.

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4.0 Results and Discussion

4.1 Adsorption behavior

In order to understand the adsorption behavior of CO_2 onto polyaspartamide, the adsorbent was experimentally studied under different adsorption conditions such as temperature, pressure and flow rates. The experimental breakthrough curve obtained for the adsorbent is shown in Figure 2. The breakthrough curve in Figure 2 was obtained at various isothermal conditions (i.e. 303, 318 and 333 K). The curves exhibited a common behavior at different adsorption temperature, constant pressure and flowrates. The general shape of the breakthrough curves for the adsorption of CO_2 onto polyaspartamide was achieved as expected; it was similar to breakthrough curves obtained for other polymer-based adsorbents reported in literature [25, 26]. The breakthrough curve explains that the amount of CO_2 captured by the adsorption sites on polyaspartamide increases with a decrease in adsorption temperature and increased operating pressure. The breakthrough curves depicted in this study showed a plot of the ratio of the final concentration at the outlet C and the inlet concentration Co against the contact time within the packed bed at different operating pressures and temperatures. The experimental conditions considered in this study are summarized in Table 1. The CO_2 adsorption breakthrough time for polyaspartamide occurred at 700 seconds at a pressure of 200 KPa and temperature of 303 K . Longer breakthrough times were observed when the temperature was increased to 318 and 333 K. This shows that the pore diameter of polyaspartamide is sufficient for CO_2 to fill in depending on the operating temperature. The saturation time for adsorption of CO_2 on polyaspartamide was quite long as deduced from the experimental breakthrough curve in Figure 2. This could be attributed to the large pore volume of polyaspartamide. The effect of feed flow rate on the adsorption of CO_2 onto polyaspartamide was investigated by operating the adsorption process at different flow rates (1.5 and 2.0 ml/s) at a constant adsorption temperature of 303 K and pressure of 2 bars as shown in Figure 3. According to the breakthrough curve in Figure 3, at higher flowrates, the packed bed adsorption column was saturated early and lower flow rates resulted in a shallower adsorption zone and longer contact time between the CO_2 and the adsorbent in the packed bed. Early breakthrough time resulted in a less CO_2 uptake by polyaspartamide. The high CO_2 adsorption capacity displayed by polyaspartamide in this study is attributed to the large

surface area of the amine grafted polyaspartamide. The Bohart-Adams and Thomas non kinetic models were used to fit the experimental breakthrough curve at 303 K. It was observed that the Bohart-Adams model gave a better fitting with the experimental data as shown in Figure 4. This means that external mass transfer dominated the overall system kinetics during the CO_2 adsorption process in this study. In order to determine the accuracy of each model explored in this study, an error function based on the normalized standard deviation adapted from a related study [27] was applied as shown in equation (1) ;

$$\% \text{ E} = \sqrt{\frac{\sum_{i=1}^{N=3}\left(\frac{Q_{exp}- Q_{mod}}{Q_{exp}}\right)^2}{N-1}} \times 100 \quad (1)$$

Where % E is the error function from the study in percentages, Q_{exp} is the average amount of CO_2 adsorbed experimentally at a given time, Q_{mod} is the amount of CO_2 adsorbed as predicted by the mathematical model and N is the total number of experimental runs.

The CO_2 capture efficiency of the adsorbent was calculated on percentage basis by dividing the equilibrium concentration of CO_2 by the initial CO_2 concentration according to Equation 2.

$$\% \quad CO_2 \text{ capture efficiency} = \frac{C_e}{C_o} \times 100 \quad (2)$$

Where C_e is the gas concentration at equilibrium and C_o is the initial concentration of the gas. The percentage CO_2 capture efficiency was obtained at all temperatures considered in this study using Equation 2 and presented in Table 3.

Table 3. CO_2 capture efficiency of polyaspartamide at different adsorption temperatures and constant pressure.

Temperature (K)	Pressure (bar)	CO_2 capture efficiency (%)
303	2	92.67
318	2	90.00
333	2	86.67

4.2 Kinetics of Adsorption

A good adsorbent is expected to have fast adsorption kinetics. More so, kinetic data of the adsorption process is another characteristic that is very important in the design of a CO_2 capture system. The Lagergen's pseudo 1st order, pseudo 2nd order and Avrami kinetic models were used to investigate the kinetics of adsorption CO_2 onto polyaspartamide as presented in Figure 5. The Lagergen's pseudo 1st and 2nd order kinetic models had some limitations with respect to the adsorption of CO_2 onto polyaspartamide. After few seconds, the Lagergen's pseudo 1st order model under-estimated the uptake of CO_2 till about 120 seconds and afterwards, CO_2 uptake was still under-estimated consistently until the adsorption process attained equilibrium. The pseudo second order model also did not perfectly fit into the experimental data. This therefore suggests that the Lagergen's pseudo 1st order model which described mainly the early stage of adsorption is applicable only under low surface coverage as previously reported in literature [28-33]. However, the best fit for the adsorption kinetics was consistently obtained at different temperatures with the Avrami kinetic model because of the model's ability to account for CO_2 adsorption by both physical and chemical adsorption as shown in Figure 6. Going by the results of the Avrami kinetic model in this study, the adsorption of CO_2 onto polyaspartamide could be described as a physiochemical process. The kinetic constant of the Avrami model is independent

of the initial concentration of CO_2. The kinetic models and their corresponding parameters are presented in Table 4. The Avrami kinetic model consistently displayed the least percentage error at all temperatures studied as seen in Table 4. Hence, it could be inferred that the kinetics of adsorption of CO_2 onto polyaspartamide was best described by the Avrami kinetic model.

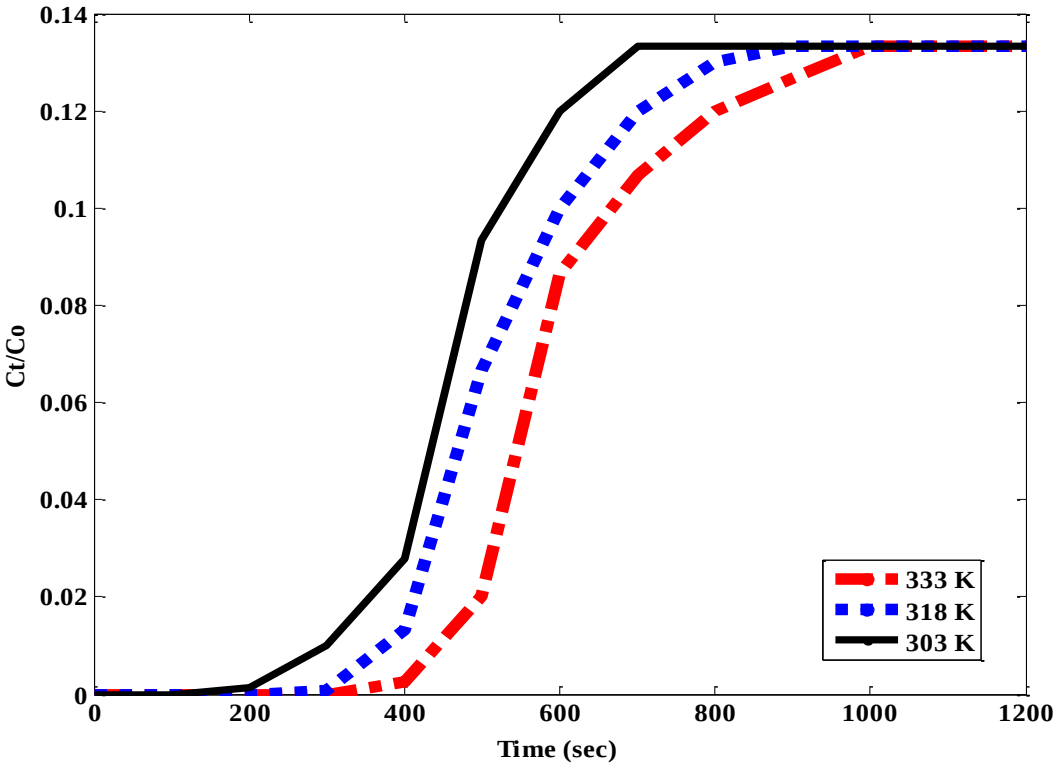


Figure 2. Experimental breakthrough curves at various adsorption temperatures, constant flow rate and constant pressure.

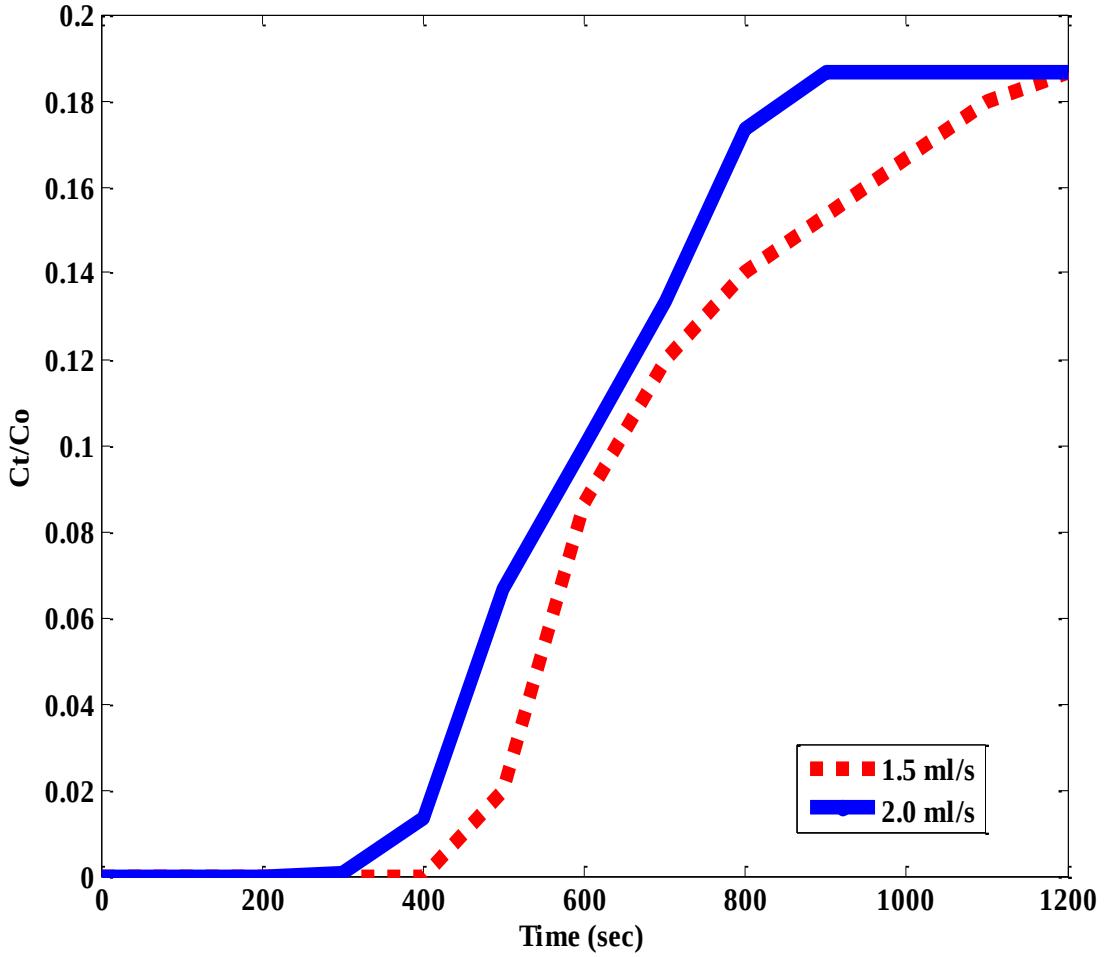


Figure 3. Effect of feed flow rate as a function of time. (Experimental conditions: feed pressure, 2 bar, and temperature 303 K).

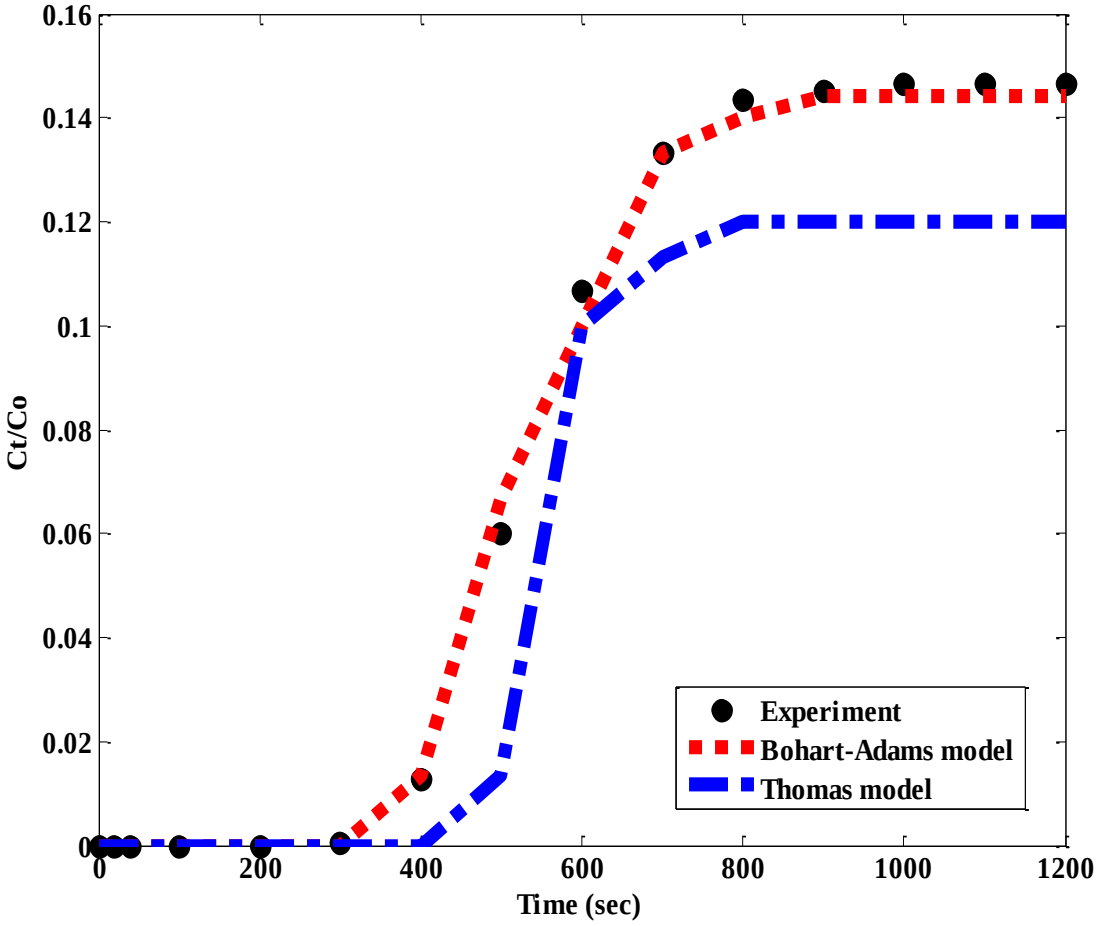
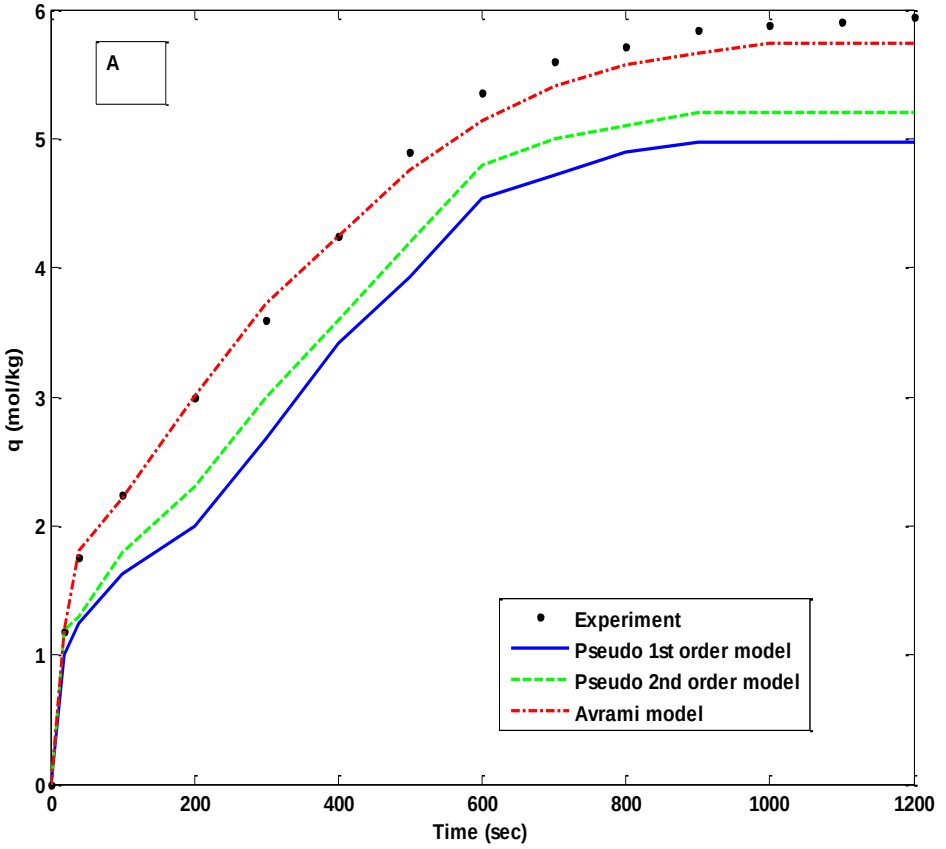
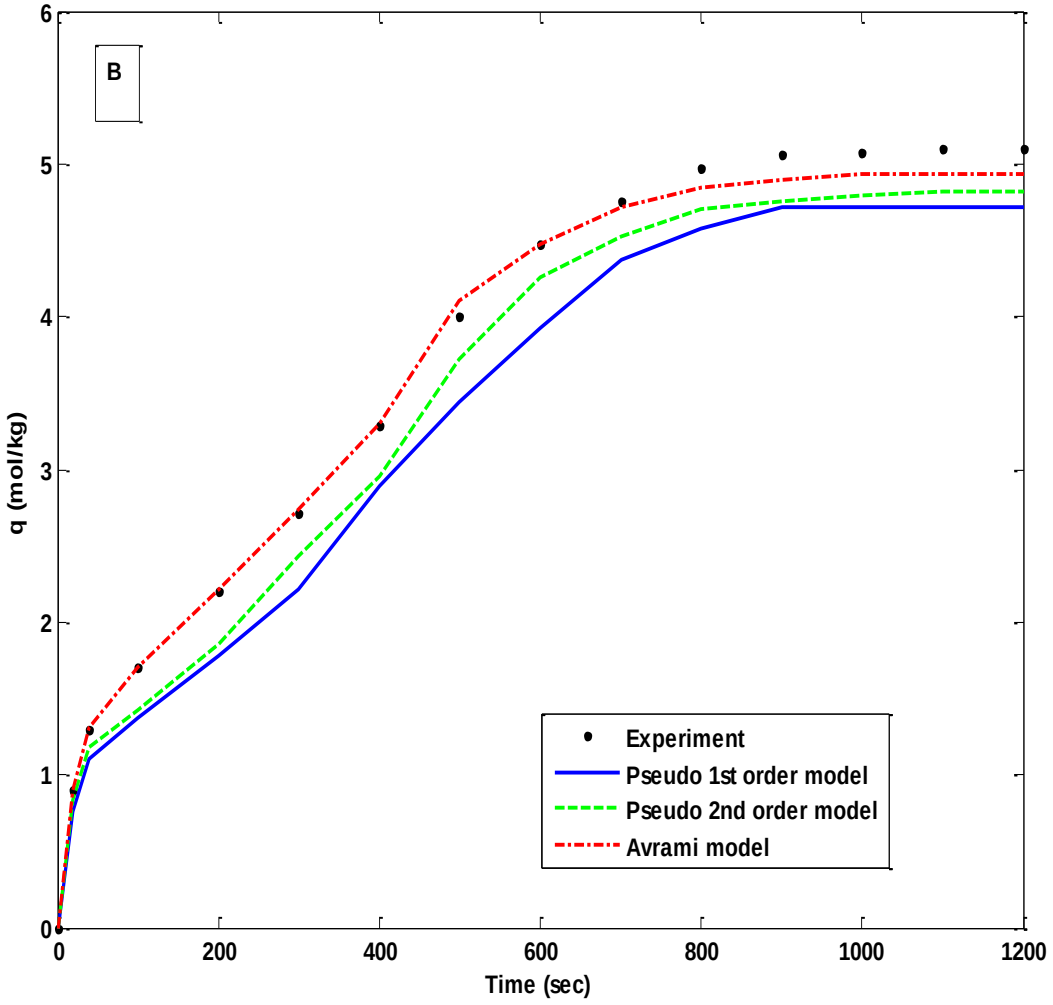


Figure 4. Experimental result versus model results. (Experimental conditions: 303 K, 2 bar)

Table 4. Kinetic model parameters for adsorption of CO_2 on polyaspartamide

Kinetic models	Parameters	303 K	318 K	333 K
Pseudo-first order model $q_t = q_e(1 - e^{-K_f t})$	Kf (s^{-1})	3.2 x 10^{-2}	3.53 x 10^{-2}	3.92 x10^{-2}
	Error (%)	1.33	5.27	2.8
	q_e (mol g^{-1})	4.97	4.72	4.37
Pseudo-second order model $q_t = \frac{q_{e^2} + tK_S}{1 + q_e K_S t}$	Ks ($gmol^{-1}s^{-1}$)	2.24 x 10^{-2}	3.14 x 10^{-2}	4.42x10^{-2}
	Error (%)	8.81	3.88	2.33
	q_e (mol g^{-1})	5.2	4.82	4.4
Avrami model $q_t = q_e[1\text{-exp}(-(K_A t^{nA})]$	K_A (s^{-1})	3.99 x 10^{-2}	4.17 x 10^{-2}	4.31x10^{-2}
	Error (%)	2.38	2.22	1.55
	q_e (mol g^{-1})	5.74	4.94	4.45
	nA	1.76	1.46	1.38




B
q (mol/kg)
Time (sec)
0
1
2
3
4
5
6
0
200
400
600
800
1000
1200
Experiment
Pseudo 1st order model
Pseudo 2nd order model
Avrami model

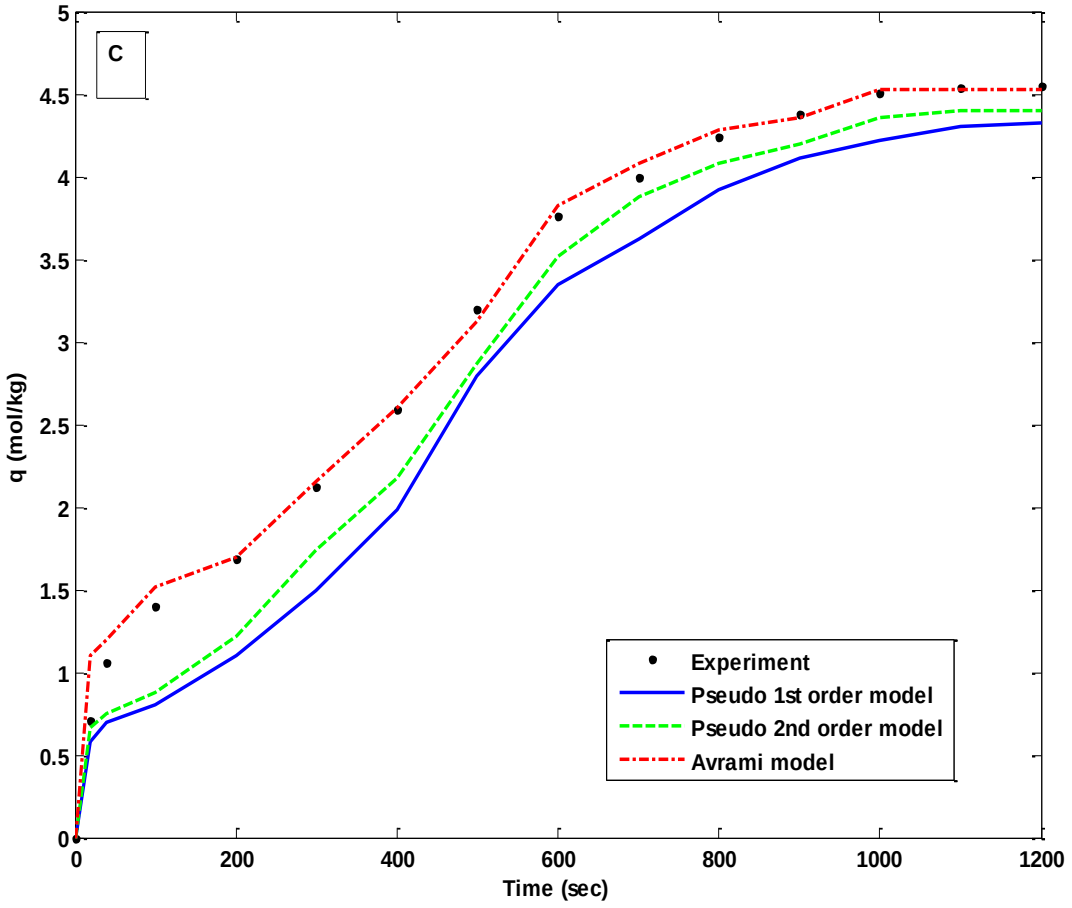


Figure 5: Experimental and predicted kinetics of adsorption of CO_2 onto polyaspartamide at (A) 303 K, 2 bar, (B) 318 K, 2 bar, (C) 333 K, 2 bar.

5. Conclusions

This study successfully investigated the adsorption behavior of polyaspartamide as an adsorbent during post-combustion CO_2 capture using kinetics and breakthrough curves under different adsorption conditions and also attempted modeling these behaviors. Based on the outcome of this study, it can be concluded that polyaspartamide is a promising adsorbent for post-combustion CO_2 capture. The breakthrough curve was successfully described using the Bohart-Adams model which could be attributed to the flexible assumptions of the Bohart-Adams

model considered in this study. From the results of the Bohart-Adams model (non-kinetic model), it can be logically concluded that mass transfer dominated the adsorption of CO_2 onto polyaspartamide. The shape of the breakthrough curve as predicted by the model was in close agreement with experimental data and equilibrium was attained at various temperatures studied after 1000 seconds as depicted in Figure 2. The Avrami kinetic model consistently and successfully described the kinetics of adsorption of CO_2 onto polyaspartamide at all temperatures studied as shown in Figure 5. This simply implies that the adsorption of CO_2 onto polyaspartamide is more of a physical than chemical adsorption process (Physiochemical). Increasing the feed (i.e. CO_2) flow rate decreased the breakthrough time because faster flow rate decreases the retention time of the gas molecules on the adsorbent within the packed bed resulting in a decreased amount of CO_2 adsorbed by polyaspartamide. This simply means that, longer breakthrough times are required for a higher amount of CO_2 to be adsorbed by polyaspartamide which subsequently results to a higher adsorption capacity.

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