Synthesis and Evaluation of SOD-ZMOF-Chitosan Adsorbent for Post-Combustion Carbon dioxide Capture

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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

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DECLARATION

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

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(Signature of Candidate)

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day               month            year
ABSTRACT

South Africa emits large amounts of carbon dioxide (CO₂) due to its reliance on coal. The emission of CO₂ needs to be reduced for clean sustainable energy generation. Research efforts have therefore been devoted to reducing CO₂ emissions by developing cost-effective methods for capturing and storing it. Amine-based absorption using monoethanolamine solvent is the most mature technique for CO₂ capture despite its huge energy consumption, corrosiveness and difficulty in solvent regeneration. However, CO₂ removal by solid adsorbents is a promising alternative because it consumes less energy, and can be operated at moderate temperature and pressure. Metal organic frameworks have received attention as a CO₂ adsorbent because they have large surface areas, open metal sites, high porosity and they require less energy for regeneration.

This research was aimed at optimizing and scaling-up SOD-ZMOF through structural modification for enhanced CO₂ adsorption by impregnating it with chitosan. Scaled-up SOD-ZMOF samples were prepared as described elsewhere and impregnated with Chitosan. Physiochemical properties obtained using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Nitrogen physisorption showed that SOD-ZMOF and SOD-ZMOF-chitosan were successfully synthesized. Qualitatively, the surface area of the SOD-ZMOF synthesized using the scaled up protocol is lower than the one prepared using the non-scaled-up protocol

XRD pattern of SOD-ZMOF showed that it was crystalline and was in agreement with literature. The XRD peaks of the SOD-ZMOF decreased after chitosan impregnation showing that chitosan was impregnated on SOD-ZMOF. The FTIR spectrum of SOD-ZMOF showed functional groups present in organic linker used to synthesize SOD-ZMOF, and that of the SOD-ZMOF-chitosan revealed the same functional groups but with disappearance of carboxylic acid functional group. N₂ physisorption showed a decrease in BET surface area and pore volume after chitosan impregnation on SOD-ZMOF as well.

Performance evaluation of the material was carried out with a demonstration adsorption set-up using a 15%/85% CO₂/N₂ mixture and as a thermal gravimetric analysis (TGA) using 100% CO₂. For both the packed-bed column and the TGA experiments, evaluation was conducted on SOD-ZMOF and SOD-ZMOF with chitosan for comparison. About 50 mg of the adsorbent was used at 25 ℃, 1 bar and 25 ml/min for the packed-bed column. For the adsorption with the TGA, 11 mg of adsorbent was used at 25 ℃, 1 bar and 60 ml/min.
SOD-ZMOF showed improved adsorption capacity after chitosan impregnation. CO$_2$ adsorption capacity of SOD-ZMOF increased by 16% and 39% using packed-bed column and TGA, respectively, after chitosan impregnation. The increase in adsorption capacity was attributed to the impregnated chitosan that has amine groups that display a high affinity for CO$_2$.

A traditional approach was used to investigate the effect of adsorption temperature and inlet gas flowrate on the CO$_2$ adsorption capacity of SOD-ZMOF-chitosan. This was done using both the packed bed column and the TGA. Temperature range of 25-80 °C and inlet gas flowrate range of 25-90 ml/min were investigated. Adsorption capacity increased with a decrease in temperature and inlet gas flowrate. For the packed-bed column, maximum of 781 mg CO$_2$/g adsorbent was obtained at 25°C, 1 bar, 25 ml/min and for the TGA a maximum CO$_2$ adsorption capacity of 23 mg/g adsorbent at 25 °C, 1 bar, and 60 ml/min was obtained.
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PUBLICATIONS


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NOMENCLATURE
ASU: Air Separation Unit
AMP: 2-amino-2-methyl-1-propanol
CO₂: Carbon dioxide
BET: Brunauer, Emmett, and Teller
CCS: Carbon Capture and Storage
DMF: Dimethylformamide
EDA: Ethylenediamine
EOR: Enhanced oil recovery
FTIR: Fourier transform infrared
GHG: Greenhouse gases
IEA: International Energy Agency
IL: Ionic liquid
MDEA: Methyltriethanolamine
MEA: Monoethanolamine
MOFs: Metal organic frameworks
N₂: Nitrogen
O₂: Oxygen
PZ: Piperazine
PSA: Pressure swing adsorption
SACCCS: South African Centre for Carbon Capture and Storage
TGA: Thermal gravimetric Analysis
TSA: Temperature swing adsorption
SOD-ZMOF: Sodalite zeolite-like metal organic framework

SOD-ZMOF-Chitosan: Chitosan impregnated Sodalite-like metal organic framework

XRD: X-ray diffraction
CHAPTER 1: INTRODUCTION

1.1. Motivation and Background

South Africa is largely dependent on coal for energy generation (Nyajowa, 2014). In 2013, it was reported that 72% South African primary energy was generated from coal and the remaining percentage was from oil, nuclear, natural and renewables (see Figure 1.1) (EIA, 2015).

![Figure 1.1: Total primary energy consumption in South Africa, 2013 (adapted from EIA (2015))](image)

To date about 90% of South Africa’s electricity needs is provided from coal (Nyajoya 2014). It is likely that coal will remain the main source of energy in the next decade because it is available, cheap and also due to lack of suitable alternatives to coal as energy source (Eskom, 2015). Coal is combusted for electricity generation. This exhausts high levels of carbon dioxide (CO$_2$) into the atmosphere. CO$_2$ is a major greenhouse gas which substantially causes the greenhouse effect which is known to be the major cause of global warming. Global warming then results to climate change and related environmental disasters. Much effort has been devoted in finding ways of reducing the amount of CO$_2$ being released to the atmosphere. Carbon capture and storage (CCS) technology is the most common and most identified way. This is because CCS makes it possible to continue using coal for energy generation while reducing the amount of CO$_2$ being released to the atmosphere (Lackner, 2009). CCS comprises three main steps. First CO$_2$ is captured from point sources such as coal power plants, cement plants and other industries that burn fossil fuels for energy source.
Second stage is transportation of CO$_2$ to storage site, and finally storage of CO$_2$ where CO$_2$ is stored in a way that will not affect the environment (Li et al., 2011).

The South African centre for Carbon Capture and Storage (SACCCS) has been established to investigate the feasibility of CCS in South Africa. SACCCS’s strategy is to develop and implement a roadmap for the implementation of CCS in South Africa by 2025 (SACCCS, 2015). In 2004, a preliminary investigation was done to determine if South Africa has potential storage sites for CO$_2$ (SACCCS, 2015). Results from this investigation showed that South Africa has potential storage sites for CO$_2$ storage.

In CCS; CO$_2$ needs to be captured first before it is stored, hence the scope of this research was focused at CO$_2$ capture. Capture is the most expensive stage in CCS (Li et al., 2011). They are three different methodologies for capturing CO$_2$ from point sources. CO$_2$ can be captured before and also after combustion of fossil fuels. When CO$_2$ is captured before combustion the method is called pre-combustion and when captured after combustion the method can be post-combustion or Oxy-combustion (Lee & Park, 2015). The difference is that in post-combustion air is used and in oxy-combustion pure oxygen is used. Thus oxy-combustion is more expensive than post-combustion because an extra stage is required to separate oxygen from air (Lee & Park, 2015). The CO$_2$ concentration in the gas stream, pressure of gas stream and type of fossil fuel are responsible in selecting the type of capture method (IPCC, 2015). This study focused on post-combustion capture. Different technologies have been developed and investigated for capture methodologies. These technologies include absorption, adsorption, and membrane separation, cryogenic and microbial technologies (Lee & Park, 2015).

Adsorptive CO$_2$ removal using solid adsorbents has been shown to be very effective. This method presents the benefits of low toxic secondary products and easy to operate (Imeteaz & Sung, 2014). Adsorption process can be carried out at low temperatures, thus it is less energy intensive compared to absorption (Imeteaz & Sung, 2014). There are a number of solid adsorbents that has been developed and investigated for CO$_2$ capture, but metal organic frameworks (MOFs) have drawn much attention over the past decade (Chen et al., 2011). This is explained in that MOFs have large surface area, adjustable pore sizes, open metal sites and less energy for regeneration. Rowsell and Yaghi (2004) defined MOFs as organic-inorganic porous solids that contain metal ions linked to organic ligands. The two assemble together to form extended frameworks through coordination bonds (Rowsell & Yaghi, 2004).
Several types of MOFs have been developed and investigated for capturing CO$_2$. One of the most recent that is reported in the literature is the zeolite-like metal organic framework (ZMOF). This is a type of MOF with zeolite-like topology. ZMOFs have been investigated for CO$_2$ capture by Chen et al. (2011). Their study focused on investigating adsorption of CO$_2$ by ZMOFs associated with Sodalite and rod topologies (SOD-ZMOF and rod-ZMOF). Chen et al. (2011) further modified the SOD-ZMOFs by incorporating some alkali metals in the framework through ion exchange. Both the SOD-ZMOF and the modified framework displayed a relatively high CO$_2$ adsorption capacity as compared to other types of MOFs which proved that SOD-ZMOF is a potential adsorbent for CO$_2$ capture.

Additionally, the properties of MOFs can be enhanced by incorporating appropriate functional groups to the MOF structure through grafting, impregnation and ion exchange to improve its CO$_2$ adsorption capacity (Imeteaz & Sung, 2014). The Amine functional group is of particular interest for incorporating in solid adsorbents. This is because the interaction between basic modified amine active sites and acidic CO$_2$ enables adsorption by covalent bonding (Yu et al., 2012). A major advantage of amine based adsorbents is that they require low heat of regeneration as compared to aqueous amines (Yu et al., 2012). Chen et al., grafted ethylenediamine (EDA) on SOD-ZMOF to enhance its adsorption capacity, and the EDA-grafted SOD-ZMOF gave a 30% increase in adsorption capacity as compared to the ordinary SOD-ZMOF (Chen et al., 2013), thus the adsorption capacity of SOD-ZMOF can be enhanced for CO$_2$ capture.

According to Shukla et al. (2012), chitosan is a bio-degradable, bio-renewable, bio-compatible and non-toxic polymer derived from chitin (Shukla et al., 2013). Chitosan is obtained from naturally occurring sources such as insects, arthropods, shellfish, shrimp, prawns, crabs and fungi (Shukla et al., 2013). Due to properties such as biocompatibility, biodegradability, high permeability, non-toxicity high viscosity, high solubility in various media, ability to form films and capability to bind with various metal ions and cost effectiveness, chitosan has gained growing interest over the past few years (Sashiwa & Aiba, 2004). The aforementioned properties have enabled chitosan to be applied for different uses in food industry, cosmetics, and agriculture, waste water treatment and biomedical (Shukla et al., 2013).

Chitosan is a green material and is the second largest most abundant polymer on earth (Ma et al., 2015) The presence of functionalities such as amine (-NH$_2$) and hydroxyl (-OH) in the
chitosan molecules provides basis for interaction with other materials (Xie et al., 2013). Therefore, of recent chitosan has been receiving great attention to be used as novel functional composite material (Shukla et al., 2013). Chitosan can be blended with porous materials to form composite chitosan modified materials (Shukla et al., 2013). Numerous works has been reported on composite modified materials (Shukla et al., 2013), but as far as could be ascertained no study on SOD-ZMOF-chitosan composite have appeared in literature.

Chitosan, being a biodegradable organic material with several anime groups depending on its degree of deacetylation, can be a green material that could be used as a substitute to synthetic liquid amine. Also, the final product; SOD-ZMOF-chitosan would have very little environmental effect. Against this background, this research was aimed at designing a composite adsorbent from SOD-ZMOF and chitosan for capturing CO₂.

1.2. Problem statement and Aim

Absorption process, with monoethanolamine (MEA) as absorbent, is the most mature technology that can be applied for post-combustion CO₂ capture (Garðarsdóttir et al., 2015). The advantage of using MEA is that it combines strongly and selectively with CO₂ and solubility process of CO₂ into MEA is relatively fast and inexpensive (Khan et al., 2016). However, the main problem that industries face with this method is corrosion as MEA is more corrosive than most secondary and tertiary amines (Pires et al., 2011). Another problem is that the process is energy intensive as most of the energy required for CO₂ capture is consumed in heating the CO₂ rich MEA in the stripper column in order to regenerate the solvent (Pires et al., 2011). This calls for efficient alternative method for CO₂ capture from point sources.

Amine based adsorbents have drawbacks such as high cost and environmental negative impacts associated with synthetic amines; making it challenging for commercial application of this adsorbents (Yu et al., 2012). This calls for an alternative material that has strong affinity for CO₂ but with less production cost and less environmental negative impacts. This work proposed chitosan as an alternative source of amine functional group to be impregnated on SOD-ZMOF.
1.3. **Research questions**

This study provided answers to the following questions:

i) Can up-scaling synthesis protocol for producing SOD-ZMOF affect physicochemical properties of the synthesized crystals?

ii) Can SOD-ZMOF-chitosan composite adsorbent be synthesized successfully?

iii) What will be the performance of the adsorbent for post-combustion CO$_2$ capture?

iv) What will be the effect of operating variables on the CO$_2$ adsorption capacity of the material?

1.4. **Objectives of the study**

This research aimed at optimizing and up-scaling the synthesis of ZMOFs (SOD-ZMOF in particular) through structural modification or formation of composite material for enhanced CO$_2$ adsorption. Also, the project explored the synergy between SOD-ZMOF and chitosan in the synthesis of a composite adsorbent for CO$_2$ capture. Specific objectives of this work were:

(i) To scale-up the synthesis of SOD-ZMOF and compare results with those from literature

(ii) To investigate the CO$_2$ adsorption capacity of the material in (i) by impregnating it with chitosan and evaluating the performance of the material for CO$_2$ capture

(iii) To investigate the effect of operating variables such as temperature and flowrate on CO$_2$ adsorption capacity of the adsorbent in (ii).

1.5. **Scope of study**

This study was limited to the scale-up of the synthesis, characterization and evaluation of the SOD-ZMOF-chitosan for post-combustion CO$_2$ capture. The study also investigated the influence of the operating variables on the adsorption capacity of the adsorbent. The study does not focus on CO$_2$ transportation and storage after storage.

1.6. **Expected outcomes**

The expected outcomes of this research were:

i) Successfully synthesized SOD-ZMOF-chitosan composite adsorbent for CO$_2$ capture
ii) Information on the performance of the adsorbent in (i) for CO₂ capture and effect of operating variables on the performance

iii) Communication of the findings journal papers, conference proceedings and in a report

References


CHAPTER 2: LITERATURE REVIEW

2.1. Introduction
This chapter discusses the CO₂ problem in detail and reviews work that has been done on reduction of CO₂ emissions. It also looks at why and how climate change is a challenge the whole world is facing today as well as the effects caused by climate change at present. The Chapter discusses the technologies, methods and materials that have been developed and investigated for reducing the amount of CO₂ being released into the atmosphere. In addition, this chapters looks at the advantages and disadvantages of developed technologies, methods and materials. This chapter concludes with a summary of all the investigated technologies, methods and materials. Figure 2.1 depicts an overview of this chapter.

![Figure 2.1: Overview of literature review](image)

2.2. CO₂ emissions
Carbon dioxide is a colourless and odourless gas that is produced from human or natural sources. CO₂ is also naturally present in the atmosphere as it is part of the earth’s carbon cycle. Additional CO₂ is also produces through human activities such as those highlighted in Figure 2.2. CO₂ produced from human activities is called anthropogenic CO₂. In the past the atmospheric sink was large enough to accommodate for additional CO₂ produced from
anthropogenic activities. However, since the beginning of industrial revolution the CO$_2$ concentration in the atmosphere has increased from 280 parts per million (ppm) by volume to 397 ppm by volume in 2014 and has continued to increase with an average of about 2 ppm annually in the last decade (IEA, 2015). The increase in atmospheric CO$_2$ concentration is known to be due to anthropogenic activities. Among many anthropogenic sources that are known to produce greenhouse gases the use of fossil fuel contributes the largest amount of greenhouse gases emissions released in the atmosphere as depicted in Figure 2.3 (Le Quéré et al, 2012). In most parts of the world, fossil fuels are the main source of energy production.

Figure 2.2 shows that 68% of greenhouse gases produced from anthropogenic activities are from the energy production sector. Out of the 68% of greenhouse gases emissions produced from energy generation; 90% of the emissions are CO$_2$ emissions (IEA, 2015). This is because when fossil fuels are combusted for energy production CO$_2$ is an inevitable product from the energy production process. About 80-85% of global primary needs are provided from fossil fuels resources (Susarla et al., 2015). In 2011, the international energy agency (IEA) predicted that the amount CO$_2$ emissions from the use of fossil fuels will be 40.2 GT by the year 2030 (Ziobrowski et al, 2016).

![Figure 2.2: Global major sources of anthropogenic sources of greenhouse gases (Adapted from EIA, 2015)](image-url)
The problem is CO$_2$ is a major greenhouse gas accounting for 80% of the impact and has drastic consequences on the environment (Freije et al, 2016). Increase in atmospheric concentration of greenhouse gases such as CO$_2$ results in a phenomenon called greenhouse effect that results in global warming. The greenhouse effect is when the temperature of the earth increase due to the trapping of heat in the atmosphere by greenhouse gases (Anderson et al, 2016). The earth’s temperature increases more than it would if the only source of warming was from direct sunlight (Anderson et al, 2016). This is because greenhouse gases absorb some of the heat that would otherwise have escaped from the atmosphere to outer space. This heat is then redirected back to the earth, thus making it warmer (Venkataramanan & Smitha, 2011). This increase in average temperature of the earth is called global warming (Venkataramanan & Smitha, 2011). The major effect of global warming is climate change (Venkataramanan & Smitha, 2011). According to Venkataramanan & Smitha (2011) as the earth is getting warmer disasters like hurricanes, floods and droughts are occurring more frequently. Other possible effects of increasing temperatures include:
- **Oceans**

The oceans serve as sink for CO$_2$, however increased atmospheric concentrations of CO$_2$ in the ocean has led to ocean acidification which changes the pH of the ocean environment (Venkataramanan & Smitha, 2011). Increased temperatures result in the ocean unable to absorb excess CO$_2$. More effects of global warming on the ocean includes rising sea levels due to thermal expansions and melting of glaciers (Venkataramanan & Smitha, 2011). Sea level rise is one of the certain effects of global warming, because of the 10 to 20 cm rise over the cause of the 20th century which was 10 times more than average rate over the previous three thousand years (Venkataramanan & Smitha, 2011). Venkataramanan & Smitha (2011) reported that the effect of sea rise will be severe in some places due to geologic factors.

- **Weather**

High temperatures speed up evaporation of water from oceans and thus increase the amount of water vapor in the air which leads to heavy rains (Wang & Chameides, 2005). Heavy rainfall is known to increase the risk of flooding. With increase in temperatures, droughts are expected to occur frequently (Wang & Chameides, 2005). Increase in temperature results in high rate of evaporation and if precipitation doesn’t replace the lost moisture from the soil then the soil will grow drier and this can affect the agricultural industry (Wang & Chameides, 2005).

- **Health**

Increase in temperatures results in outbreaks of vector borne diseases by lengthening the season during which vectors are active and expanding the geographic range of tropical mosquito-borne diseases, such as malaria, dengue fever and yellow fever (Wang & Chameides, 2005). It is reported that malaria kills one to two million people annually (Wang & Chameides, 2005).

This are just a few possible effects caused by increased temperatures and it is evident that effort has to be made in order to find ways of preventing the worst from happening due to increasing atmospheric concentration of CO$_2$. It is of great significance to find possible ways of reducing the amount of CO$_2$ concentration in the atmosphere.
2.3. Reduction of CO₂ emissions

It is important to identify factors that contribute to high CO₂ emissions, in order to minimize them. The modified Kaya identity (Equation 2.1) provides direct relationship between anthropogenic CO₂ emissions represented by C and human population (P), economic development indicated by the gross domestic product, (GDP), energy production (E), carbon-based fuels used for energy production (C) and CO₂ sinks, S<sub>CO₂</sub> (Bachu, 2008; Pires et al, 2011).

\[ C = P \frac{E}{GDP} \frac{C}{E} - S_{CO₂} \]  

(2.1)

According to Equation 2.1, increase in anthropogenic CO₂ emissions is directly proportional to the human population increase per capita GDP, the energy intensity of the economy (E/GDP) and carbon intensity of the energy system (C/E) (Bachu, 2008; Pires et al, 2011). Based on equation 2.1, there are 5 ways in which anthropogenic CO₂ emissions can be reduced (Bachu, 2008; Pires et al, 2011). The first two ways involves the reduction of population and economic outputs which are not a realistic solution due to policy implementation (Bachu, 2008). The third and fourth ways involves increasing energy efficiency and switching completely or partially to renewable energy such as wind, solar, nuclear, biomass to replace coal (Bachu, 2008; Pires et al, 2011). However, the high cost of renewable energy compared to the abundance of fossil fuels availability is delaying the introduction of green renewable energy (Bachu, 2008; Pires et al., 2011). Furthermore, the use of biomass could lead to conflict with other land and water uses as well as food production and forestation (Bachu, 2008). The fifth term, S<sub>CO₂</sub> representing CO₂ sinks involves the continuous use of coal for energy generation and the use of CCS technology to stabilize CO₂ emissions (Bachu, 2008; Pires et al., 2011).

Pires et al (2011) reported that coal will remain the main source of energy in this century. Maintaining the CO₂ emissions from fossil fuels is the most indicated technology to stabilize atmospheric CO₂ emissions (Pires et al, 2011). This could be achieved using a technology called carbon capture and storage (CCS). CCS involves CO₂ capture from fixed generation sources, transporting it to storage site and storing it in geological sites (Pires et al, 2011). Point sources include power plants, cement manufacturing plants, refineries, iron and steel industries as well as petrochemical industries. CCS is considered the only technology that can reduce CO₂ emissions from the power generation industry (Cebrucean et al, 2014). The IEA
(2014) reported that CCS can reduce total energy production related emissions by 14% by the year 2050 (IEA, 2014).

2.4. **Carbon Capture and Storage**

CCS is the most identified and commonly used technology for stabilizing CO₂ emissions in the atmosphere. The main advantages of CCS are that it is deployable in a number of industries and it allows the continued use of fossil fuels for energy production with low CO₂ emissions (Stanley, 2014). It involves CO₂ capture at point sources of generation such as cement factories, steel production and coal power plants; compressing it to a supercritical fluid to be transported and then storing it in geographical sites (Zhang & Huisingh., 2017). Figure 2.3 illustrates an overview of the CCS process. CCS comprises of three main steps as observed in figure 2.4: CO₂ capture, transportation and storage.

![Diagram illustrating concept of carbon capture and storage](image)

**2.4.1. CO₂ transport and storage**

After capturing CO₂, it is compressed to liquid and supercritical fluid before it is transported and stored. CO₂ is transported by either pipelines, trucks or ship to a place where it will be stored (Zhang & Huisingh., 2017). Table 2.1 gives the advantages and disadvantages of the aforementioned CO₂ transportation options.
Table 2.1: Pros and Cons of CO$_2$ transport options (Adapted from Zhang & Huisingh., 2017)

<table>
<thead>
<tr>
<th>Transport option</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trucks</td>
<td>Good for transportation of small amount of CO$_2$</td>
<td>• High CO$_2$ leakage risk</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• High Transport costs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Only small amount of CO$_2$ can be transported per load</td>
</tr>
<tr>
<td>Pipelines</td>
<td>• Has been used in industry for more than 40 years</td>
<td>• Pipeline integrity</td>
</tr>
<tr>
<td></td>
<td>• Large amount of CO$_2$ can be transported per load</td>
<td>• Flow assurance</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Safety and operational considerations</td>
</tr>
<tr>
<td>Ships</td>
<td>• Low transport costs</td>
<td>• Extra costs may be incurred as CO$_2$ needs to be</td>
</tr>
<tr>
<td></td>
<td>• Low CO$_2$ leakage risk</td>
<td>compressed first</td>
</tr>
<tr>
<td></td>
<td>• Large amount of CO$_2$ can be transported per load</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Low CO$_2$ leakage risk</td>
<td></td>
</tr>
</tbody>
</table>

When CO$_2$ is transported by trucks it is to be stored in land, when transported by pipelines it can be stored in either land or sea and when transported by ship it is stored in sea (Zhang & Huisingh., 2017). CCS keeps CO$_2$ out of the atmosphere by capturing it from power plants and injecting it in deep reservoirs that contain fluids for thousands of years (Zhang & Huisingh., 2017).

CO$_2$ storage involves injecting captured CO$_2$ from point sources into geological sites (Zhang & Huisingh., 2017). Thus captured CO$_2$ does not go back to the atmosphere therefore reducing the amount of CO$_2$ that is being released into the atmosphere. The captured CO$_2$ could be purely for the purpose of storage or for utilization. A mature example of utilization of CO$_2$ is the enhanced oil recovery (EOR) from depleted oil reservoirs (Zhang & Huisingh., 2017).
EOR is a process whereby CO\textsubscript{2} is used to recover oil. EOR has been practiced in Canada at the Weyburn oilfield since 1954 and also in USA at the SACROC oilfield since 1947 (Zhang & Huisingh., 2017). This research work is limited to only Carbon capture.

2.4.2. Carbon Capture

Before CO\textsubscript{2} is transported and stored it needs to be captured from different point sources. CO\textsubscript{2} capture is the first stage. In power plants, flue gas is the CO\textsubscript{2} containing gas mixture produced during electricity generation. CO\textsubscript{2} must be separated from this gas mixture before it is stored or utilized. CO\textsubscript{2} capture is the most expensive stage, approximately about two thirds of the total cost of CCS process (Li et al., 2011). In addition CO\textsubscript{2} capture can reduce the efficiency of the plant by about 14% and it increases the amount of electricity used in the plant by 30-70% depending on the type of capture technology used, plant type and fuel used (Cebrucean et al, 2014). As such, there are various technologies that have been developed and investigated.

CCS can be performed using three different methodological routes for capturing CO\textsubscript{2}: pre-combustion, oxy-combustion and post-combustion. In all three methodologies CO\textsubscript{2} must be efficiently separated from other gases before storage.

2.4.2.1. Techniques used to capture carbon dioxide

2.4.2.1.1. Pre-combustion

In this capture method, CO\textsubscript{2} is removed from process before combustion. Pre-combustion is primarily applicable to gasification plants where fuel (coal or biomass) mixed with oxygen is converted to mainly CO and H\textsubscript{2} (Li et al., 2011). The CO formed is reacted with steam in a catalytic convertor to produce CO\textsubscript{2} and more H\textsubscript{2} (Li et al., 2011). CO\textsubscript{2} is then separated from H\textsubscript{2} by a number of technologies such as absorption, adsorption or membrane separation (Li et al., 2011). Pure hydrogen is combusted with air in the power plant. The advantage of this method over post-combustion is that it achieves higher CO\textsubscript{2} concentration and pressure at outlet stream, which makes CO\textsubscript{2} capture much more efficient, it also requires lower energy requirements (Li et al., 2011). However this method is disadvantaged by high investment costs and public resistance to new technology (Thorbjornsson et al, 2015; Li et al, 2011). Figure 2.5 depicts an overview of a process for CO\textsubscript{2} capture by pre-combustion.
2.4.2.1.2. Oxy-combustion

Oxy-combustion is done using pure oxygen produced using a cryogenic air separation or membranes (Perrin et al., 2015). Combustion with pure oxygen is associated with high temperature when compared with combustion with air. CO\(_2\) is captured after the combustion stage. Combustion products are CO\(_2\) and water (H\(_2\)O). The two are separated by condensing water. CO\(_2\) rich gas is recycled to reduced temperatures. The CO\(_2\) recovery in the output stream is relatively high with values exceeding 95% and produces CO\(_2\) with purity of about 99.999 % (Perrin et al., 2015). A major advantage of oxy-combustion over post-combustion is that no nitrogen oxides are formed when using the former technology (Perrin et al., 2015). However, oxy-combustion is relatively expensive due to costs associated with obtaining pure oxygen from air. The cryogenic distillation process is quite expensive and is energy intensive. Figure 2.6 depicts the process of CO\(_2\) capture using oxy-combustion.
2.4.2.1.3. Post-combustion

Like oxy-combustion, CO₂ is removed after combustion of coal. The major difference from oxy-combustion is that for post-combustion air is used during the combustion stage. This technology is applied to fossil fuel burning power plants. Example of such plants is coal fired and oil fired power plants (NETL, 2015). In this coal fired power plants, CO₂ is captured from flue gas after combustion of fossil fuel. This capturing method can be used when gas contains low concentration of CO₂. Main advantage of post-combustion is that it can be easily integrated into existing power plants with few modifications of the combustion process compared to pre-combustion and oxy-combustion (Wang et al., 2011). Post-combustion produces CO₂ which can be applied in enhanced oil recovery, urea production and food/beverage industry (Garðarsdóttir et al, 2015). In this study, post-combustion method was investigated for CO₂ capture. Figure 2.7 depicts the process of CO₂ capture using post-combustion method.

![Diagram of CO₂ capture process](image_url)
2.4.3. Conversional technologies used in capturing CO₂

There are a lot of technologies that have been developed and investigated for capturing CO₂. These technologies include absorption, cryogenic distillation, membranes and adsorption and are discussed in detail in this section.

2.4.3.1. Absorption

Absorption is a process in which molecules dissolve in liquid solvent (Keller & Staudt, 2005). The liquid solvent in which molecules dissolve in is called an absorbent. Molecules undergoing absorption are taken up by a volume of the bulk phase (liquid solvents). Using of liquid solvents as absorbents has practical advantages for large scale gas separation. Advantages include technical maturity and ability to treat large volume of gas (Li et al., 2017). Absorption is accompanied by desorption where the dissolved molecules are separated from the solvent. This is known as stripping. Figure 2.8 depicts the process of adsorption and stripping.

![Figure 2.7: Overview of Post-combustion capture (Adapted from Lee & Park, 2015)](image)
Absorption process can be physical or chemical depending on the type of absorbents used. In physical absorption, CO$_2$ is absorbed at high pressure and low temperature and desorbed at low pressure and high temperature (Yu et al, 2012). The absorbents used are non-reacting. Absorbents used influence separation through interaction between target gas and absorbents. Physical absorption is more effective when separating gases across large pressure difference or with high concentration of targeted gas (Yu et al, 2012). The advantages of physical absorption are low toxicity, low vapor pressure and less corrosion solvent compared to chemical adsorption. In chemical absorption, absorbents used are reactive. Absorbents effect separation through some type of chemical reaction between the targeted gas and absorbent. Chemical absorption is effective for smaller pressure difference situations that require larger binding energies (Yu et al., 2012). Yu et al reported that chemical absorption is usually operated at a pressure of 1 bar. Absorption and desorption temperatures vary at ranges of 40-60 °C and 120-140 °C respectively (Yu et al., 2012).

There are a number of different solvents that have studied and investigated for CO$_2$ capture. However the absorption process with amines is the most commonly used process in industry for post-combustion CO$_2$ capture (Khan et al, 2016). Monoethanolamine (MEA) is the most common and is a commercial solvent due to its low cost, high CO$_2$ selectivity and availability.
In coal fired power plants, flue gas containing CO$_2$ gas from combustion stage is contacted with an amine in an absorber column at relatively low temperatures. The CO$_2$ is absorbed by dissolving in the amine. The CO$_2$-loaded amine solvent is pumped into a stripping column, where it is heated to regenerate the solvent and release CO$_2$ (Yu et al., 2012). The hot solvent is then recycled back to the absorber column through a heat exchanger. The heat exchanger cools the hot solvent to the absorption column temperature and preheats the loaded MEA going to the stripper (Yu et al., 2012).

Several studies have been conducted where amine and amine blended solvents were investigated for CO$_2$ capture. Khan et al (2016) did a comparative study of four different amine solvents for CO$_2$ absorption. The solvents investigated were MEA, 2-amino-2-methyl-1-propanol, methyldiethanolamine (MDEA) and piperazine (PZ) (Khan et al, 2016). CO$_2$ absorption study was conducted in a packed column at temperature range of 298-313 K and CO$_2$ partial pressure ranging from 10 to 15 kPa. Khan et al (2016) investigated the influence of solvent concentration, gas flowrate and solvent flowrate on CO$_2$ absorption. Three different mass compositions (10, 20 and 30 wt. %) were investigated for each of the four solvents. The authors observed that the specific rate of absorption increased with increase in amine concentration and CO$_2$ partial pressure for each solvent. CO$_2$ loading also increased with increase in mass concentration of amine in aqueous solution (Khan et al, 2016). CO$_2$ absorption performance of the investigated solvents followed the trend: PZ>MEA>AMP>MDEA and in terms of specific absorption rate and regeneration performance the following trend was observed: AMP>MDEA>PZ>MEA (Khan et al, 2016).

Nwaoha et al (2016) reported on the CO$_2$ absorption using a highly concentrated tri-solvent blend containing 2-amino-2-methyl-1-propanol (AMP), piperazine (PZ) and (MEA). The authors varied individual concentrations of AMP and PZ but the total concentrations of two solvents remained constant in the mixture (Nwaoha et al, 2016). This was done to minimize the possibility of precipitation. AMP-PZ-MEA tri solvent blends showed slightly higher equilibrium CO$_2$ loading compared to that of standard 5 Kmol/m$^3$ MEA (Nwaoha et al, 2016). All blends showed improved CO$_2$ adsorption capacity of about 29.1% - 38% higher as compared to that of just standard MEA (Nwaoha et al, 2016).

The advantage of using amine technology is that it is a mature process and has been commercialized for decades (Yu et al., 2012). In spite of this advantage, CO$_2$ absorption
using amine solvents has several drawbacks. Inefficiencies with amine based absorbent include:

- **Loss of amine**

Due to their volatility, amines can be lost through emissions. Amine solvent is lost through vaporization, entrainment and chemical degradation (Luis et al., 2012). Even though traps are typically used to minimize amine loss, amine emissions in a form of aerosols are still a major challenge (Dutcher et al., 2015). Aerosols can escape these traps causing concern to the environment and resulting in increased amine required to make up for the lost amine (Dutcher et al., 2015).

- **Amine degradation**

Amine degradation is a very serious concern that generally occurs in two methods (Dutcher et al., 2015). The first one is oxidative degradation where amines are generally fragmented into toxic compounds such as amides, organic acid and ammonia (Dutcher et al., 2015). The second method is thermal degradation that usually occurs in the stripper column where high temperature conditions tend to produce larger amine chain molecules (Dutcher et al., 2015). Both methods of degradation results in the formation of compounds with poor CO₂ capture properties, lower capacities and slower kinetics than the original amine (Dutcher et al., 2015). The degradation products also have effect on the operating of equipment as they cause corrosion of equipment (Dutcher et al., 2015).

- **Equipment corrosion**

The main problem that industries face with this technology is corrosion as amine solvents especially MEA is more corrosive than most secondary and tertiary amines (Pires et al., 2011). In coal fired power stations, CO₂ is separated from flue gas. Flue gas contains oxygen that reacts with amine to produce corrosive degradation products (Pires et al., 2012).

- **Cost of regeneration**

The Regeneration step can increase the operating cost of capture plant by about 70% (Ziobrowski et al., 2015). CO₂ absorption using aqueous amine based absorbents results in formation of ammonium salts such as ammonium bicarbonate and ammonium carbonate (Tu et al., 2012). CO₂ needs to be separated from the ammonium salts before it is transported and stored (Dutcher et al., 2015). The process of separating CO₂ from ammonium salts is called
striping. The main purpose of striping is to regenerate amine solvents so it can be recycled and reused for absorption again. Absorption products (ammonium salts) are thermally decomposed in order to regenerate and separate solvent from CO$_2$ (Dutcher et al., 2015). Ammonium salts are heated in order to liberate CO$_2$. Ramdin et al (2012) reported that the heat input to remove 1 ton of CO$_2$ by using 30% MEA aqueous solution is about 2.5 to 3.6 GJ. Yu et al (2012) reported that regeneration of CO$_2$ using 30 wt% to 40 wt% MEA aqueous solution is about 3.3 to 3.01 GJ/ton CO$_2$. Favre (2011) reported that about 3.5 GJ/ton is required to regenerate CO$_2$ from amine solvent.

Other drawbacks of this absorption using amines are low CO$_2$ loading capacity and large equipment size (Yu et al, 2012). In an effort to overcome these drawbacks, researchers look into improving absorbents and operations (Yu et al., 2012) by combining amines and developing new absorbents. Ionic liquids (IL) are one of the new solvents that researchers develop to absorb CO$_2$. IL can be applied in both physical and chemical absorption. However the major drawback of using ILs for CO$_2$ absorption is their high viscosity (Yu et al., 2012).

2.4.3.2. Cryogenic distillation process

Cryogenic distillation is a gas separation technique that uses distillation at extremely low temperatures and high pressure (Leung et al., 2014). The difference between this technology and the conventional distillation is that cryogenic distillation separates gaseous mixtures instead of liquid mixture (Leung et al., 2014). For CO$_2$ capture, flue gas is cooled to sublimation temperatures and CO$_2$ in its solid state is separated from other light gases present in flue gas and then compressed at high pressures of about 100-200 atmosphere (Leung et al., 2014). Cryogenic distillation can recover about 90-95% CO$_2$ from flue gas (Leung et al., 2014). This CO$_2$ separation method is reported to be energy intensive as it operates at low temperature and high pressures (Leung et al., 2014). Figure 2.9 depicts an overview of separation by cryogenic distillation.
Cryogenic distillation can be applied in post-combustion CO₂ capture where CO₂ and water (H₂O) are separated from gas on a basis of dew and sublimation points. The main advantage of cryogenic method is the simultaneous separation of CO₂ and H₂O from flue gas in the absence of using solvents and high pressures. The main concern with using this method is that the water content in feed stream of cooling units should be minimized or reduced to prevent plugging by ice or high pressure drop during operation (Pires et al., 2011). The advantage of cryogenic distillation is that no absorbents are required and CO₂ can be captured at atmospheric pressure (song et al., 2012). According to Song et al (2012), the major challenge with cryogenic distillation is the expected high cost of cooling.

Song et al (2012) developed a novel system of cryogenic distillation for CO₂ capture. The authors investigated the influence of temperature and flowrate on CO₂ recovery and process performance. Their research was based on the stirring cooler technology. This technology presents several advantages including high reliability and high efficiency (Song et al., 2012). Song et al (2012) demonstrated that the stirring cooler system can separate CO₂ efficiently. A CO₂ recovery of 96% with 1.5 MJ/Kg CO₂ energy consumption was achieved by song et al (2012) using the cryogenic distillation technology.
Song et al (2014) optimised the novel cryogenic CO$_2$ capture process discussed above using response surface methodology (RSM). The authors used three levels and variable central composite design to investigate the influence of capture conditions on performance focusing on CO$_2$ recovery and energy consumption (Song et al., 2014). Investigated parameters were idle operating time (range of 3-5 h), flowrate (range 1-3 L/min) and FPSC temperature (range 30-10°C). Optimization results showed that these parameters had significant effect on CO$_2$ recovery and energy consumption (Song et al., 2014). The optimum conditions were found to be idle operating time of 3.9 h, gas flowrate of 2.16 L/min and FPSC temperature of -18°C. Song et al (2014) found that the CO2 recovery of 95.2 % and energy consumption of 0.52 MJ/captured CO$_2$ at the aforementioned operating conditions. The energy consumption was reduced after optimization.

2.4.3.3. Membrane

Membranes separate species by selectively permeating certain components of a mixture faster over others through a thin barrier (Leung et al., 2014). Flue gas enters the membrane and the membrane only allows CO$_2$ gas molecules to pass through while retaining other gases (Anantharaman et al., 2016; Leung et al., 2014). The CO$_2$ rich stream is called permeate and the CO$_2$ lean stream is called the retentate. Figure 2.10 depicts a flow diagram of CO$_2$ separation by membrane. The driving force behind membrane separation could be concentration, pressure and chemical potential gradient. Several types of membranes have been developed and investigated; these include metallic, ceramic and polymeric membranes (Hofs et al, 2015).
Membrane separation is advantageous over other method of separating gases. Their advantages include (Quan et al., 2017; Leung et al., 2014):

- It is a simple and passive operation with no moving parts.
- It is an environmentally friendly method without the use of toxic chemicals
- Less energy intensive because separation of gases do not require phase change
- It has higher separation efficiency as compared to equilibrium based processes

In membrane separation, molecules move or permeate through the membrane through variety of transport driving forces. The type of transport is largely dependent on sizes of pores or free volume elements in the membrane and the size of molecules to be separated. Table 2.2 gives the common types of membrane transport mechanism.
Table 2.2: Membrane transport mechanisms (Adapted from carbon capture: beyond 2020, 2010)

<table>
<thead>
<tr>
<th>Pore size (Å)</th>
<th>Transport mechanism</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;200</td>
<td>Convective flow</td>
<td>No separation-typical gas filter</td>
</tr>
<tr>
<td>$\lambda/D &gt; 1$ (20-1000)</td>
<td>Knudsen flow</td>
<td>Very low separation</td>
</tr>
<tr>
<td>5-10</td>
<td>Surface flow</td>
<td>An example of this is micro porous carbon with 5-7Å pore size for separation of H$_2$ from hydrocarbons</td>
</tr>
<tr>
<td>&lt;5</td>
<td>Molecular sieving</td>
<td>Carbon membranes with &lt; 5Å pore. It is very selective</td>
</tr>
<tr>
<td>Dense</td>
<td>Solution diffusion</td>
<td>Commercial polymeric gas separation membranes. Used mainly for H$_2$ separation, Air separation, CO$_2$ separation from natural gas.</td>
</tr>
<tr>
<td>permanent pores</td>
<td>Ion transport ceramic</td>
<td>Under development for ultrapure H$_2$, O$_2$</td>
</tr>
</tbody>
</table>

For gas separation applications such as capturing CO$_2$ from flue gas, solution diffusion transport mechanism is of interest. An example of membranes with such mechanism is polymeric membrane. Polymeric membranes are typically limited to the relationship between selectivity and permeability. Polymeric membranes present several advantages such as low cost, high performance separation, easy to synthesis and mechanically stable (Pires et al, 2011). For CO$_2$ capture using post-combustion, polymeric membranes cannot be applied without cooling the flue gas. This is because high temperatures rapidly destroy the membrane (Pires et al, 2011). Polymeric membrane can also be applied in pre-combustion in steam reforming reaction to separate CO$_2$ from H$_2$. In oxy-combustion, polymeric membranes can be applied to produce oxygen rich streams from air (Pires et al, 2011). The application of polymeric membranes in pre-combustion and oxy combustion is an attempt to increase amount of CO$_2$ captured in outlet stream (Pires et al, 2011).

Major drawbacks of polymeric membranes such as thermal stability resulted in the development of ceramic membranes (Nwogu et al, 2015). Unlike polymeric membranes, ceramic membranes can capture CO$_2$ at high temperature (Lackner & West, 2007). Other
advantages of ceramic membranes are mechanical stability and higher chemical stability which results to longer lifespan of membrane (Hofs et al, 2015). Several studies have been done where ceramics membranes have been applied for CO\textsubscript{2} capture. Nwogu et al (2015) reported on the performance evaluation of inorganic ceramic membranes for CO\textsubscript{2} gas separation. Daramola et al (2016) reported on the successful synthesis and characterisation of Nano composite Sodalite ceramic membrane via pore plugging hydrothermal synthesis for pre-combustion CO\textsubscript{2} capture.

In spite of the many advantages of membrane separation technology for CO\textsubscript{2} capture, there are several disadvantages presented by this technology. The main problem is that treatment of large flowrate of flue gas emitted from coal fired power stations requires large membrane area which results in increased costs of the membrane capture technology (Pires et al, 2011). Another major problem with this technology is that it requires large energy compensation and expensive compression equipment for post-combustion capture, thus making the technology expensive (Pires et al, 2011). The membrane technology is still under development (Leung et al., 2014).

\textbf{2.4.3.4. Adsorption}

This process is believed to be the most suitable for post-combustion capture (Yu et al, 2012). Adsorption is a process where molecules (liquid, gas or solid) adhere to the surface of a material (Keller & Staudt, 2005). In the case of gas adsorption, when a gas makes contact with a solid; it can be taken up by the solid. The solid that takes up the gas is referred to as the adsorbent and the gas adsorbed to the solid as the adsorbate (Keller & Staudt, 2005). The reverse of adsorption where the gas detaches from the adsorbent is called desorption (Keller & Staudt, 2005). Adsorption is considered advantageous over other capture methods because it requires low energy for regeneration, fast kinetics, increased loading capacity and it can operate at low temperature as well as pressure (Saxenaa et al, 2014). Adsorption process requires for molecules to make strong contact with solid surface. Depending on the interaction energy and strength between adsorbate and adsorbent, adsorption can either be physisorption (physical) or chemisorption (chemical) (Keller & Staudt, 2005).

\textit{Physisorption and chemisorption}

Physisorption is also known as physical adsorption. If the interaction between the adsorbent and adsorbate is weak, then physisorption is taking place (Dutta, 2009). In this process there
is weak binding between the adsorbent and adsorbate. Forces of physisorption are van der Waal forces and for electrostatic force between adsorbate and surface of adsorbent (Dutta, 2009; Suzuki, 1990). The main advantage of physisorption is that it requires lower energy to separate the gas molecules from the adsorbent (Dutta, 2009). Examples of adsorbents used in physical adsorption include activated carbon and zeolites.

Chemisorption process is also chemical adsorption. Where binding between the solid adsorbent and adsorbate is strong chemical bond (Dutta, 2009). Chemisorption requires high energy to regenerate adsorbent as compared to physisorption (Dutta, 2009). The increased energy required to release gas from adsorbent contributes to energy costs. Table 2.3 provides some of the difference between chemical and physical adsorption.

Table 2.3: comparison of physisorption and chemisorption (Dutta, 2009; Keller & Staudt, 2005; Lowell & Shields, 1998)

<table>
<thead>
<tr>
<th>Physical adsorption</th>
<th>Chemical adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small heat of adsorption</td>
<td>Large heat of adsorption</td>
</tr>
<tr>
<td>Usually occurs at low temperature and adsorption decreases with increase in temperature</td>
<td>Occurs at high temperature and adsorption increases with increase in temperature</td>
</tr>
<tr>
<td>Caused by intermolecular forces</td>
<td>Caused by chemical bond</td>
</tr>
<tr>
<td>Results in multimolecular layer</td>
<td>Results in unimolecular layer</td>
</tr>
<tr>
<td>Reversible</td>
<td>Irreversible</td>
</tr>
<tr>
<td>Fast kinetics</td>
<td>Slow kinetics</td>
</tr>
</tbody>
</table>

Adsorption Isotherms

When an adsorbent comes in contact with adsorbate, adsorption process occurs, after some time equilibrium will be established between amount of adsorbate adsorbed and amount of adsorbate remaining (not adsorbed). The relationship that occurs in equilibrium is described by adsorption isotherms. Equilibrium is usually described in terms of partial pressure (gas) or concentration (liquid) and amount adsorbed (Donohue & Aranovich, 1998). Therefore adsorption isotherm is a graph that represents the relationship between the amounts of adsorbate adsorbed on the surface of adsorbent with changing pressure at constant temperature. Adsorption isotherms are significant because they are used to calculate the specific surface area and pore size of adsorbents.
There are different types of adsorption isotherms and there are 6 main adsorption isotherms (type I to type VI). Figure 2.11 depicts an illustration of these adsorption isotherms. Type I isotherms also known as Langmuir isotherm is representative of micro-porous adsorbents (Balbuena & Gubbins, 1993; Donohue & Aranovich, 1998). Type II and type III isotherms are representative for non-porous adsorbents with weak and strong adsorbate-adsorbent attractive forces respectively (Balbuena & Gubbins, 1993; Donohue & Aranovich, 1998). Type VI and V isotherms is representative of meso-porous adsorbents with strong and weak adsorbate-adsorbent attractive forces respectively (Balbuena & Gubbins, 1993). Type V is generated when adsorbate condenses in mesopores of solid adsorbents. Type VI is a rare isotherm which is generated for strong adsorbate-adsorbent attractive forces, it occurs usually when the temperature of the adsorbate (gas) is close to melting point (Balbuena & Gubbins, 1993).

![Adsorption Isotherms Diagram](image)

**Figure 2.11: Classification of adsorption isotherms (Taken from Donohue & Aranovich, 1998)**

**Adsorption Mechanism**

Adsorption process occurs due to the presence of unbalanced forces on the surface of the adsorbent. These unbalanced forces have a tendency to attract and adsorb molecules that come in contact with the adsorbent surface. This is explained by attractive forces that exist between the adsorbent and the molecules they adsorb (adsorbate). Figure 2.12 illustrates a clear demonstration of the adsorption mechanism of CO₂ from flue gas. As depicted by
Figure 2.12, a flue gas stream is passed through an adsorbent. The adsorbent attracts and adsorbs CO$_2$ molecules while other gas molecules pass. After CO$_2$ molecules are adsorbed, the adsorbent is subjected to either pressure change or temperature change in order to desorb CO$_2$ and regenerate the adsorbent so it is recycled.

When adsorbent is regenerated by changes in temperature, the process is known as temperature swing adsorption (TSA). The column is usually heated by hot gas such as nitrogen in order to remove impurities from the adsorbent (Tili et al., 2009). TSA is an attractive adsorption mechanism because it is potentially less energy intensive due to the moderate heat of adsorption, there is no volatility of solid adsorbents and moderate temperature of regeneration is required (Joss et al., 2017). Figure 2.13 depicts a diagram of the overview of how TSA works.
When adsorbent is regenerated through change in pressure, the process is called pressure swing adsorption (PSA). PSA is a cyclic process where adsorption is carried out in relatively high pressures while desorption occurs at lower pressure (Gomes & Yee, 2002). When PSA is used adsorption is done at pressures higher than atmospheric (Tlili et al., 2009). The major advantage of PSA is the absence of high energy associated with regeneration stage (Riboldi & Bolland, 2015). Several studies have been done on CO₂ capture using PSA (Gomes & Yee, 2002; Tlili et al., 2009; Riboldi & Bolland, 2015). Figure 2.14 depicts a diagram of the overview of how PSA works.

Figure 2.13: Overview of TSA process

When adsorbent is regenerated through change in pressure, the process is called pressure swing adsorption (PSA). PSA is a cyclic process where adsorption is carried out in relatively high pressures while desorption occurs at lower pressure (Gomes & Yee, 2002). When PSA is used adsorption is done at pressures higher than atmospheric (Tlili et al., 2009). The major advantage of PSA is the absence of high energy associated with regeneration stage (Riboldi & Bolland, 2015). Several studies have been done on CO₂ capture using PSA (Gomes & Yee, 2002; Tlili et al., 2009; Riboldi & Bolland, 2015). Figure 2.14 depicts a diagram of the overview of how PSA works.
The desorbed CO$_2$ by TSA, PSA or other desorption methods can be utilized in other processes that require CO$_2$ or stored in ways that will not affect the environment. The adsorbent is regenerated and used again to capture more CO$_2$. The process of adsorption and desorption continues for a number of cycles depending on the type of adsorbent. Figure 2.15 depicts process flow diagram of adsorption and desorption by either TSA or PSA.

**Modes of adsorption operation**

Adsorption can be operated in either a batch flow or continuous flow system. In a batch flow system the quantity of adsorbent is mixed with specific amount of mixture containing the adsorbate. Mixing is continued until the adsorbate in the mixture is reduced to a desired level. The adsorbent is then removed and either discarded or regenerated. Batch flow systems are usually used for small volume of adsorbate.

In Continuous adsorption operation there is continuous contact between adsorbate and adsorbent. There are three types of continuous adsorption systems which are fixed/packed-bed, moving bed and fluidized bed. This study investigates adsorption using a fixed/packed-bed adsorption system. In a fixed/packed-bed adsorption column, adsorbent is loaded inside
the column and the gas mixture containing CO₂ enters the column at bottom. As the gas moves through the column it gets adsorbed. After adsorption is complete the saturated adsorbent is then passed to a regeneration column where CO₂ is separated from the adsorbent using either temperature or pressure changes as discussed. Figure 2.15 depicts a schematic diagram of a fixed/packed-bed adsorption system.

![Figure 2.15: Overview of fixed/packed-bed adsorption system (Adapted from Rashidi & Yusup, 2016)](image)

*Adsorbents materials*

Adsorbents are materials used to adsorb or capture other substance from a mixture. There are important factors for solid adsorbents used in the adsorption process should have so adsorption can be effective.

Selectivity is a very important characteristic and property. Adsorbents should be designed in a way that it is selective to adsorbate of interest from mixtures. A selective adsorbent allows its pores to be filled with adsorbate of interest, which is then released for adsorbent to be reused. Selectivity of the adsorbent could be governed by the difference in affinity, rate of diffusion and particle size. These may determine the selectivity of the adsorbent individually or collectively (Dutta, 2009).

Where selectivity is governed by rate of diffusion; different component in the mixture are likely to diffuse into the pallet of the adsorbent at different rates and this gives rise to selectivity for gas molecules that diffuse faster to be adsorbed quickly (Dutta, 2009). This kind of selectivity is also called kinetic selectivity (Dutta, 2009).
Selectivity can also be governed by molecule size and shape of different components in the mixture as this may vary (Dutta, 2009). Hence molecules that have molecular size greater than the pore size of the adsorbent will not be able to enter the pores of the adsorbent (Dutta, 2009). Only molecules that have a molecular size smaller than the pore size of the adsorbent will enter the pores (Dutta, 2009).

Other factors include adsorption capacity, amount of energy required to regenerate the adsorbent. Adsorbent should be designed in a way to minimize the energy required for regeneration. Particle size, porosity, structural strength and stability are also factors to be considered for a good adsorbent (Dutta, 2009). A good adsorbent must be highly porous and have a narrow particle distribution (Dutta, 2009). Good adsorbent should have large number of adsorption sites that the adsorbate can bind in which is achieved by high surface area of adsorbent. High surface area made possible by designing small particles of adsorbents (Dutta, 2009).

*Adsorbents commonly used for CO₂ capture*

Adsorption process provides an alternative to CO₂ capture over the above aforementioned methods. This is because adsorption method for gas removal is less energy intensive, process has the ability to operate at low to moderate temperature and pressure. Most importantly, adsorption process is more economic due to versatility of adsorbents (Ackley et al, 2003).

An effective CO₂ adsorbent is one that has cheap raw materials, fast kinetics, high CO₂ adsorption capacity, high selectivity towards CO₂, low heat capacity and has thermal as well as mechanical stability (Yu et al, 2012). A lot of adsorbents have been proposed and investigated for CO₂ capture. The most common of these adsorbents are discussed.

**Zeolites**

Zeolites, three dimensional materials, are crystalline aluminosilicates structures which are porous (Lee & Park, 2015). Mostly due to presence of aluminium in the silicate structure, CO₂ can be adsorbed by zeolites. Zeolite materials can be natural or synthetic. Synthetic zeolites are synthesized by hydrothermal reaction in an autoclave (Lee & Park, 2015). Examples of synthetic zeolites that are commercially used are type A and type X zeolites (Suzuki, 1990). This material consists of metal ions such as Li, Na and Al that are surrounded by four oxygens in tetrahedron geometry (Lee & Park, 2015). These metal ions influence the heat of adsorption (Lee & Park, 2015). The shape and size of zeolites can be tuned to specific dimensions that allow selective passage of different gases. The tuning of the shape and size of
zeolites depends on the atoms and structures used for the material (Carbon Capture: Beyond 2020, 2010). There are number of different zeolites that vary with chemical and physical properties. Properties such as molecular pore size, strength, selectivity and cation are not the same for different zeolites (Lenntech, 2015). Zeolites are currently the largest class of commercially available adsorbents.

There three main applications of zeolites in industry. These applications include catalysis, ion exchange and gas separation (Lenntech, 2015). In catalysis, zeolites are used as catalysts for several reactions. An important example is isomerization, cracking and hydrocarbon synthesis. Hydrated cations within zeolite pores are loosely bounded to zeolite framework. These cations can be exchanged with other cations in aqueous media. An example of this application is where zeolite-like metal organic framework is ion exchanged with alkali metals.

Due to their ability to adsorb polar compounds, zeolites have long been considered as best candidates for separation and purification of gases (Ackley et al., 2003). Here the porous structure of zeolites is used to sieve molecules according and size. Molecules of particular size are allowed to enter the pores of the zeolite.

Zeolites are one of the most widely investigated adsorbents for CO₂ capture. Hefti et al (2015) investigated zeolites 13X and ZSM-5 for Adsorption equilibrium of binary mixtures of carbon dioxide and nitrogen. The aforementioned authors first investigated single component adsorption isotherms of CO₂ and N₂ over a range of temperatures from 25 °C to 140°C. Hefti et al (2015) then investigated binary adsorption equilibrium measurements at temperatures of 25°C and 45°C on both zeolite 13X and ZSM-5. The measured equilibrium was compared with predictions by adsorption models and application of ideal adsorbed solution theory and real adsorbed solution theory for non-ideal behaviour (Hefti et al., 2015). This work was limited in the description and interpretation of the behaviour of adsorption on the aforementioned zeolites. The authors found that zeolite ZSM-5 behaves close to ideal over the entire temperature and pressure investigated, while zeolite 13X demonstrated non-ideal behaviour with increased pressure which motivated the use of real adsorbed solution theory to describe the binary mixture adsorption data (Hefti et al., 2015).

The disadvantages of using zeolites as adsorbents for CO₂ capture are that the CO₂ adsorption capacity and CO₂/N₂ selectivity are very low. Another drawback of zeolites is that in the presence of moisture CO₂ adsorption capacity declines because of the hydrophilic nature of
zeolites. This then results in high regeneration temperatures thus large energy required (Yu et al., 2012). A major disadvantage is that the design and tunability of zeolites restricts the aforementioned zeolite to a particular pore size which results to less molecule application (Eddaoudi et al., 2014).

**Silica materials**

Pure silica is naturally a material that is inactively non-polar, however once it has a hydroxyl functional group its surface becomes polar and hydrophilic (Suzuki, 1990). In literature, work has been reported on synthesis and modification of silica materials for CO$_2$ capture. In most studies, silica supports are incorporated with amine functional groups or metal nanoparticles in order to enhance CO$_2$ adsorption capacity (Lee & park, 2014). Silica materials are cheap, have large micro and meso pores and can CO$_2$ adsorption can be done at medium of low temperature and pressure (Lee & Park, 2014). However in spite this advantages, silica materials adsorb moisture easily which results in poor performance for CO$_2$ adsorption. Another drawback is that this material requires high energy during desorption (Lee & Park, 2014).

Xu et al (2002) reported on Polyethylenimine-modified mesoporous molecular Sieve of MCM-41 (MCM-41-PEI) by loading PEI onto MCM-41 as silica adsorbent for CO$_2$ capture. CO$_2$ adsorption-desorption runs were measured in a flow system using a microbalance that measures weight change. MCM-41-PEI had an adsorption capacity of 215 mg CO$_2$ / PEI at 348 K and 1 bar which were 24 times that of MCM-41 and 2 times that of PEI alone (Xu et al., 2002). Adsorbent could adsorb CO$_2$ at very low concentrations and was found to be stable when cyclic operations were conducted (Xu et al., 2002).

Hung et al (2017) investigated CO$_2$ capture using polyamine-immobilized mesostructured silica. The authors investigated the role of amine modification and the existence of poly (ethylene oxide) surfactant molecules on surface properties of mesoporous silica on CO$_2$ uptake using 2 dimensional heteronuclear correlations (HETCOR) solid-state NMR technique. The investigated silica materials showed a CO$_2$ adsorption uptake of 4.43 mmol CO$_2$/g adsorbent (Hung et al., 2017).

**Activated carbon**

This is a non-graphite form of carbon from natural raw materials such as wood, saw dust, nut shell, coal and lignite (Dutta, 2009; Suzuki, 1990). In order to produce activated carbon, the
aforementioned raw materials are mixed with alkali metals and heated at temperatures of 500-900 °C (Dutta, 2009). The product is washed, filtered and dried (Dutta, 2009).

This adsorbent is widely used to purify gases, remove impurities from drinking water and also absorbs poisons from digestive systems in medical application (Carbon Capture: Beyond 2020, 2010). Commercially available activated carbons are produced in two forms; powder form or granular form (Dutta, 2009; Suzuki, 1990).

Activated carbon is suitable post-combustion capture due to their properties such as low cost, wide availability, high porosity, high thermal stability, low sensitivity to moisture and stability in adsorption-desorption cycles (Yu et al, 2014, Rashidi & Yusup, 2016). Activated carbon is considered more superior for post-combustion capture than zeolites because of its hydrophobic property that prevents an additional step of moisture removal prior to CO₂ adsorption (Rashidi & Yusup, 2016). Activated carbon are physical adsorbents and have weak interaction with CO₂, thus they have a lower heat of adsorption compared to zeolites (Rashidi & Yusup, 2016; Montagnaro et al., 2015).

Montagnaro et al (2015) investigated post-combustion CO₂ capture on two commercial activated carbons which are filtrasorb 400 (F600–900) and nuchar RGC 30 (RGC30). The aforementioned activated carbons were studied at temperatures 303, 323 and 353 K. Montagnaro et al (2015) carried equilibrium and kinetic CO₂ adsorption tests in fixed bed apparatuses on filtrasorb 400 and nuchar RGC 30 at different temperatures and CO₂ inlet concentrations in order to provide insights on the role played by microstructure features of activated carbon on CO₂ adsorption capacity. F600–900 exhibited high CO₂ adsorption capacity under typical flue gas conditions which the authors explained by narrower pore size distribution.

Sexenaa et al (2014) investigated activated carbon as adsorbents for CO₂ capture and results showed that activated carbon has potential to be used for capturing CO₂. In spite of its advantages, there are several drawbacks associated with using activated carbon to capture carbon dioxide. The major drawback is that activated carbon is negatively affected by NOₓ, SOₓ and H₂O. This is a major disadvantage because the flue gas produced from post-combustion contains these compounds. Other disadvantages are low CO₂ adsorption capacity at mild conditions and wide variety of raw materials (Spigarelli & Kawatra, 2013).
Metal Organic Frameworks (MOFs)

MOFs are organic-inorganic porous solids that contain metal ions linked to organic ligands which assemble together to form an extended framework through coordination bonds. According to Rowsell and Yaghi (2004), a porous solid is called a metal organic structure when it displays a geometrically well-defined structure, strong bonding that provides robustness, linking units that are available for modification by organic synthesis. The solid should be highly crystalline as this allows precise structural characterization by diffraction methods (Rowsell & Yaghi, 2004). MOFs are advantageous over the aforementioned adsorbents due to higher large surface area, regular pore distribution, pore size can be enlarged by increasing the size of linker while keeping the same structure type and finally; properties of MOFs can be modified by the possibility of modifying the linker with various organic groups while keeping the same structure (Devic & Serre, 2009).

MOFs synthesis

Synthesis of various MOFs

They are several methods that have been investigated for MOFs synthesis. These methods include hydrothermal, electrochemical, solvent free, ionothermal, solvothermal and microwave synthesis. The standard method for synthesizing of MOFs is the solvothermal reaction starting from metal precursor and organic ligand at temperatures between room temperatures and 400 degrees. This is better illustrated by the Equation 2.2

\[ \text{Metal precursor} + \text{organic linker} = \text{metal organic framework} \]  

Metal source can be a metal salt such as halide, nitrate or hydroxide. Also metal source can also be metal which is further oxidized during reaction by adding oxidizing agents such as ad nitric acid or perchloric acid in reaction vessel. In this case the inorganic subunit will form in original place during the course of the reaction.

Reactants are mixed in high boiling polar solvents such as water, amides and alcohol. Water is usually the solvent of choice but amides, alcohols or their mixture is commonly used (Devic & Serre, 2009). Products produced are either one, two or three dimensional metal organic structures. The metal organic structure needs to be filtered and dried from this wet process. This needs to be done carefully because, due to high surface areas and porosity of MOFs, they may easily carry 50 to 150 weight percent of the occluded solvent (Czaja et al,
2009). It is therefore advisable to first remove the adsorbed solvent under gentle conditions in terms of temperature and pressure before high thermal activation (Czaja et al., 2009). Synthesis of MOFs is affected by many important parameters including temperature, concentration of metal salt and organic ligand, the extent of solubility of reactants on solvent as well as the PH of the solution.

**Structure of MOFs and characterization**

**Structure of MOFs**

MOFs are both crystalline and highly porous materials. Choice of building blocks (metal and organic linker) determines the structure and properties of MOFs. Figure 2.16 depicts a structural picture of MOF. As can be seen in Figure 2.16, the structural picture of MOF where the structure contains metal centres as well as organic linkers.

![Figure 2.16: Overview of metal organic framework (taken from University of Crete, 2001)](image)
Characterization of MOFs

After synthesis, MOFs are characterized in order to identify their different properties such as textual properties, the morphology, surface chemistry, pore volume, pore size and surface area. Different techniques are used for different properties. These techniques are summarized below include X-Ray diffraction (XRD), Scanning electron microscope (SEM), Thermal gravimetric analysis (TGA), Fourier Transform Infrared spectrum (FTIR) and Brunauer-Emmett-Teller method (BET).

XRD is one of the most important tools used in solid state chemistry characterization. This characterization technique is used for two main purposes; for determination of textual properties and also for determination of whether powder is crystalline or amorphous. XRD is based on the constructive interference of monochromatic x-rays and the crystalline sample (Practical Analytical, 2015).

TGA provides thermal stability of sample by measuring the change in chemical and physical properties of materials. It measures this as a function of increasing temperature or as a function of weight or time. TGA also measures thermal decomposition patterns.

FTIR Identifies unknown materials in the sample and determines the amount of components in a mixture

BET is a standard method of determining surface area of materials from standard nitrogen adsorption isotherms. The surface area of the material is determined by the physical adsorption of the nitrogen gas on the surface of the solid.

Applications of MOFs in CO₂ capture

MOFs can be applied in many different areas. A few of these areas include gas purification, gas storage, and catalysis and gas separation. In this study MOFs are applied for gas separation.

In gas separation the gas mixture usually contains components having concentrations in the same order of magnitude. Currently industrial technologies for gas separation are cryogenic, membrane, absorption and adsorption techniques. Absorption using monoethanolamine is the commonly used method in industry, however this process possess drawback with the major one being that regeneration of solvent is quite expensive as explained in previous sections. Adsorption using porous materials such as activated carbon, zeolites, carbon nanotubes, silica
gel, molecular sieves and MOFs is a promising alternative (Kupple et al., 2009). These materials are chosen based on adsorption capacity of adsorbent as well as selectivity of the material to adsorbate than the aforementioned materials (Kupple et al., 2009). MOFs are very promising for gas separation because of their large surface area, adjustable pore sizes, open metal sites and less energy for regeneration (Chen et al., 2011). One example of MOFs application in gas separation is carbon dioxide separation from gases such as hydrogen, nitrogen and methane by adsorption where MOFs are considered as CO$_2$ adsorbents. There are a number of different MOFs that have been investigated for capturing CO$_2$. The next Section below discusses some of the types of MOFs that have been applied for gas separation in CO$_2$ capture.

**MOFs for CO$_2$ capture**

Since the discovery of MOFs, researchers have synthesized various types of MOFs for the purpose of capturing CO$_2$. This includes fluorinated metal organic frameworks (F-MOFs), MOF-505 and HKUST-1 MOF, Mg-based MOF-74 and ZMOFs (Lee & Park, 2017). Other MOFs for Carbon dioxide capture are amino functionalized metal organic framework, light weight metal organic framework and nitrogen containing metal organic framework. According to Saha et al (2012) F-MOFs are synthesized using perfluorinated polycarboxylate ligands with porous surface and exposed to fluorine atoms for carbon capacity storage.

Saha et al (2012) investigated all the aforementioned MOFs and found that they can physically adsorb CO$_2$ at ambient temperatures and pressure. The CO$_2$ adsorbed by these MOFs can be removed at room temperatures and materials can be reused as an adsorbent again. The drawback of the aforementioned materials is that the CO$_2$ loading capacity is not very high and considerable efforts must be made for better carbon dioxide storage (Saha et al, 2012).

Millward & Yaghi (2005) reported on MOFs with exceptionally high capacity for CO$_2$ storage at room temperature. Table 2.4 depicts the nine MOFs with their surface areas reported by Millward & Yaghi (2005). The MOFs reported by Millward & Yaghi (2005) have exceptionally high surface area. MOF-177 was reported to have a CO$_2$ adsorption capacity of 33.5 mmol CO$_2$ / g adsorbent at room temperature and 35 bars which is much greater than adsorption capacity to that of zeolite 13X (Millward & Yaghi, 2005).
Table 2.4: MOFs examined for CO₂ storage capacity (Millward & Yaghi, 2005)

<table>
<thead>
<tr>
<th>Type of MOF</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF-2</td>
<td>345</td>
</tr>
<tr>
<td>IRMOF-11</td>
<td>2096</td>
</tr>
<tr>
<td>MOF-505</td>
<td>1547</td>
</tr>
<tr>
<td>IRMOF-3</td>
<td>2160</td>
</tr>
<tr>
<td>MOF-74</td>
<td>816</td>
</tr>
<tr>
<td>IRMOF-6</td>
<td>2516</td>
</tr>
<tr>
<td>CU₃(BTC)₂</td>
<td>1781</td>
</tr>
<tr>
<td>IRMOF-1</td>
<td>2833</td>
</tr>
</tbody>
</table>

Llewellyn *et al* (2008) reported on the CO₂ uptake of Metals Organic Frameworks MIL-100 and MIL-101. The maximum CO₂ loading of MIL-100 and MIL-101 obtained by Llewellyn *et al* (2008) was 18 and 40 mmol CO₂/g adsorbent respectively at a temperature of 304 K and a pressure of 5 Mpa.

Bao *et al* (2011) reported on a magnesium-based metal organic framework, also known as Mg-based MOF-74 for CO₂ capture. A volumetric adsorption unit was used to measure the CO₂ adsorption equilibra and kinetics on Mg-based MOF (Boa *et al*., 2011). Mg-based MOF-74 synthesized by Boa *et al* (2011) had a surface area of 1174 m²/g and CO₂ adsorption capacity of 8.61 mmol CO₂/g adsorbent at 298 K and 1 bar. The CO₂ adsorption capacity of Mg-based MOF-74 was significantly high compared to that of zeolite 13X under the same operating conditions.

*Zeolite metal organic framework (ZMOFs)*

ZMOFs are a unique subset of MOFs with zeolite like framework topologies impressive properties like tunability and rational design for a number of applications (Eddaoudi *et al*., 2007). According to Chen *et al* (2011), the main difference is that in ZMOFs, organic linkers replace oxygen and metal ions replace tetrahedral coordinated Si or Al atoms found in zeolites. ZMOFs are negatively charged frameworks and because of this allows for tuning of pore through extra-framework cations exchange. Thus ZMOFs have the potential to be tuned and enhance host (interaction with specific guest molecules) (Al-Maythalony *et al*., 2014). ZMOFs can be mesoporous, however unlike mesoporous silica they exhibit crystalline framework (Devic & Serre, 2009). ZMOFs exhibit distinctive properties including: accessible
extra-large cavities, exceptional chemical stability and potential to be applied in many fields (Al-Maythalony et al., 2014). There is a diverse nature of ZMOFs due to the conditions of synthesis as well as what is known as structure directing agents (SDA) which is basically a template. Different types of ZMOF are produced depending of the type of SDA used. Examples of this include SOD-ZMOF and rho-ZMOF where SOD and rho refers to the topology of the ZMOF.

**Synthesis of ZMOFs**

The easiest way to describe the synthesis of ZMOF is a solvothermal reaction given by:

\[
\text{Indium nitrate hydrate + 4, 5- Imidazoledicarboxylic acid = ZMOF} \quad (2.3)
\]

The two reactants in equation 2.2 are mixed with a SDA in order to yield a type of ZMOF. The SDA used to yield SOD-ZMOF is imidazole and 1, 3, 4, 6, 7, 8-hexahydro-2H-pyrimidine [1, 2-α] pyrimidine (HPP) yields rho-ZMOF. In Figure 2.17, different SDAs were added to reaction 2 to yield different ZMOFs with different templates. SOD-ZMOF has a diameter of approximately 9.6 angstroms (Å) (Eddaoudi et al., 2014). This diameter is large enough to allow CO₂ molecules with a diameter of 3.3Å to penetrate (Eddaoudi et al., 2014).

![Figure 2.17: Formation of different ZMOFs due to the use of different SDA’s](image)
Carbon dioxide capture by Zeolite like metal organic frameworks (ZMOFs)

Chen et al (2011) investigated ZMOFs, rho-ZMOF and SOD-ZMOFs as CO$_2$ adsorbents. They investigated the effect of ion exchange on SOD-ZMOFs adsorption capacity. SOD-ZMOF was ion exchanged with group 1 metals (Li$^+$, Cs$^+$, Na$^+$, and K$^+$) cations. SOD-ZMOF showed no significant changes in textual properties after ion exchange (table 2.5). The carbon dioxide adsorption capacity of SOD-ZMOF was compared to that of most commonly investigated material ZIF (ZIF-8) and the CO$_2$ adsorption capacity of ZIF-8 was far less compared (30mg/g adsorbent) to SOD-ZMOF (53mg/g adsorbent). Although the surface area of SOD-ZMOF was smaller than that of ZIF-8 (table 2.5), the former has a much superior adsorption capacity. All ion exchanged alkali cations exhibited improved CO$_2$ adsorption capacity than the prepared sample without ion exchange alkali metals. The K$^+$-SOD ZMOF exhibited the highest CO$_2$ capacity which was 15% higher than the as prepared SOD-ZMOF followed by Na$^+$ and then Li$^+$ (Chen et al, 2011).

Table 2.5: Textual properties of ZMOFs (adapted from Chen et al (2011))

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m$^2$/g)</th>
<th>Volume of pore (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$ ion-exchanged SOD-ZMOF</td>
<td>345</td>
<td>0.16</td>
</tr>
<tr>
<td>K$^+$ ion-exchanged SOD-ZMOF</td>
<td>363</td>
<td>0.16</td>
</tr>
<tr>
<td>Na$^+$ ion-exchanged SOD-ZMOF</td>
<td>373</td>
<td>0.17</td>
</tr>
<tr>
<td>SOD-ZMOF</td>
<td>375</td>
<td>0.16</td>
</tr>
<tr>
<td>Rho-ZMOF</td>
<td>816</td>
<td>0.34</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>1450</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Composite MOFs for CO$_2$ capture

In order to improve adsorption capacity and selectivity, adsorbents are chemically modified on the surface of solid. As mentioned in the previous section, MOFs are very promising adsorbents due to their unique chemical and physical properties. Their properties can be further improved or enhanced by various means. This includes grafting, change in organic
linkers, ion exchange and impregnation of suitable active material (Imteaz & Sung, 2014). Imteaz and Sung (2014) defines composite adsorbents as porous materials with multiple phases which have at least one continuous phase. MOFs composites have large improvements in synthesis kinetics, morphology, stability, physiochemical properties and potential applications (Imteaz & Sung, 2014). MOFs composites have been receiving attention due to various applications including CO₂ adsorption.

- **Ionic liquid based adsorbents**

Ionic liquids (IL) are environmentally friendly solvents which exhibits great potential for CO₂ capture (Dai et al, 2015). IL have great potential for CO₂ capture due to their many unique advantages such as high thermal stability, strong soluble capacity for CO₂, non-flammable, high CO₂ solubility, non-volatile, negligible vapour pressure and wide liquid range. Aki et al (2007) found that CO₂ solubility is affected by type of anion and various alkyl in the cation, but solubility is strongly influenced by anion (Gupta et al., 2012). Muldoon et al. (2007) expanded the investigation and found that IL containing fluoroalkyl chain as either cation or anion have improved CO₂ solubility compared to less fluorinated IL (Gupta et al, 2012). IL investigated for CO₂ capture are room temperature ionic liquids (RTIL), task specific ionic liquid (TSIL) and supported ionic liquid (SIL) (Dai et al., 2015).

In SIL, IL impregnate the pores of porous supports (adsorbents). The two most concerns when it comes to the use of IL are cost and viscosity. SIL reduce the cost and viscosity of IL used because the amount of IL is less compared to RTIL and TSIL. This provides an important economic benefit for the application of SIL.

For SIL, IL can be supported by different types of porous materials. Since the discovery of SIL for CO₂ capture; a lot of experimental and theoretical work has been done on different IL supported by various types of porous materials.

Simulation studies have been done to establish the potential of ionic liquid impregnated MOFs for CO₂ capture. Molecular and atomistic simulations were done by Chen et al. (2011) and Gupta et al. (2012) to investigate CO₂ capture on MOF supported IL adsorbents. Both authors used IRMOF-1 as support but they used different types of IL. Results of this studies showed that the anion MOF supported IL adsorbents selectively adsorbs CO₂ from a N₂/CO₂ mixture, the selectively of the composite adsorbent is generally higher and might be potentially useful for CO₂ capture (Chen et al, 2011). Atomistic simulation was done to
investigate CO$_2$ capture in IL supported by MOFs (ZIF-71 and Na-rho-ZMOF) in order to investigate how hydrophobic and hydrophilic framework can affect CO$_2$ adsorption capacity. Gupta et al. (2013) observed that at a particular pressure CO$_2$ was more adsorbed than N$_2$ in both membranes.

IL based adsorbents are very good for CO$_2$ capture. In spite all the advantages associated with ionic liquids, their major disadvantage is that they are very expensive. So far, from most literature only simulation work has been done in investigating MOF supported IL for CO$_2$ capture. Experimental work still needs to be done so as to validate the simulation work.

- **Amines based adsorbents**

   Amine based adsorbents solids that are chemically modified by adding amine to the solid support. These adsorbents have been widely studied and they exhibit an advantage due to high CO$_2$ adsorption capacity. This is based on the fact that CO$_2$ is acidic and amine is basic, so the two reacts with one another. Other advantages of amine based adsorbents include high rate of adsorption and desorption, high ability to tolerate moisture and high selectivity for CO$_2$ in a mixture of gases (Yu et al, 2012). According to the type of amine and solid support, amine based adsorbents can be categorized as amine impregnated or amine grafted adsorbents (Yu et al, 2012).

   Chitsiga et al (2015) reported synthesis and performance evaluation of amine grafted poly-succinimide (PSI) adsorbent referred to as polyaspartamide (PAA) for post-combustion CO$_2$ capture. The authors investigated the effect of grafting water soluble amines on PSI. TGA was used to measure the adsorption capacity of the synthesized adsorbent. Grafting water soluble amine on PSI resulted in an increase in adsorption capacity. PAA showed a highest adsorption capacity of 44 mg CO$_2$/ g adsorbent at 40°C and 1 bar.

   Chen et al (2013) did an experimental investigation on SOD-ZMOF grafted with ethylenediamine (ED) for CO$_2$ capture. The authors’ grafted SOD-ZMOF with ED. Chen et al (2013) characterized SOD-ZMOF before and after amine grafting using XRD, FTIR, elemental analysis and BET. The surface area and pore volume of the grafted SOD-ZMOF decreased from 375 m$^2$/g to 347 m$^2$/g and 0.16 cm$^3$/g to 014 cm$^3$/g respectively. This showed that the grafting of ED was successful. Grafting SOD-ZMOF with ED resulted in a 30% increase in adsorption capacity. The work done by Chen et al (2013) also showed high CO$_2$
selectivity with nitrogen (N₂) and the grafted SOD-ZMOF showed outstanding stability of CO₂ adsorption desorption measurements than the original SOD-ZMOF (Chen et al., 2013).

Amines based adsorbents are strong potential for CO₂ capture due to the acid-base interaction between the weak acidic CO₂ gas and weak basic amines. However amine based adsorbents have drawbacks such as high cost and the environmental impact associated with synthetic amines; making it challenging for this adsorbents to commercialize (Liu et al., 2013). This calls for an alternative material that has strong affinity for CO₂ but which is also less expensive and has less impact on the environment. This work proposes the use of a material called chitosan to replace synthetic liquid amines.

- **Chitosan based adsorbents**

Ma et al. (2015) defined chitosan defined as a natural occurring bio-compatible, bio-degradable, bio-renewable and non-toxic co-polymer composed of glucosamine and acetyl glucosamine. This polymer is derived from chitin which is the second most plentiful natural polysaccharide (Shukla et al., 2013). Chitin which is a biopolymer produced by many different living organisms (Rinaudo, 2006). It produced from sources from nature such as insects, shellfish, crabs, fungi, arthropods and crustacean shells (Rinaudo, 2006). Naturally chitin occurs as three types (α, β and γ − structures). The third type (γ − chitin) seems to just be a combination of the α − structure and β −structure rather than a third allomorph. α −chitin is the most abundant and it is found in walls of yeast and fungal cells, shrimp cells, crab tendons and cells as well as insect cuticle. β −chitin is rare and is found in association with proteins in squid pens (Rinaudo, 2006). The structure of chitin illustrated in Figure 2.18 is compact and this disallows it to be soluble in most solvents. Therefore there is a need for chitin to be transformed into chitosan (Rinaudo, 2006).

![Figure 2.18: Structure of chitin (Taken from Shukla et al, 2013)](image-url)
Chitosans are advantageous due to the fact that they are produced from plentiful renewable resource (chitin). Properties of chitosan include viscosity, solubility in various media, ability to form films and capability to bind with various metal ions (metal chelation) (Shukla et al, 2013). Chitosan is produced from chitin under alkaline conditions or by enzymatic hydrolysis. Acetate moiety is removed from chitin under alkaline conditions through hydration in order to produce chitosan (Shukla et al, 2013). Chitosan is a polymer that consists of amine and hydroxyl functional groups (See Figure 2.19). Due to the presence of these functional groups, chitosan can be applied in many fields as well as be incorporated with other materials to improve performance.

![Figure 2.19: Structure of chitosan (Taken from Shukla et al, 2013)](image)

Due to its unique properties, chitosan has been applied to industries such as wastewater treatment, food industry, cosmetics, and agriculture and biomedical. In the biomedical industry, chitosan has been found to be a good candidate for gene therapy, cell culture and tissue engineering due to its excellent properties.

The presence of functionalities such as amine (-NH$_2$) and hydroxyl (-OH) in the chitosan molecules provides basis for interaction with other materials. Therefore, the recent chitosan has been receiving great attention to be used as novel functional composite material. Chitosan composite can be produces either by chemical modification or physical modification. Physical modification is the easiest way and is mostly done by physically mixing (Shukla et al, 2012).

Chitosan composite materials have received interest in the wastewater industry. Recently in 2013, Xie et al (2013) studied on chitosan modified zeolite as an adsorbent for the removal of different wastewater pollutants. Xie et al (2013) synthesized a zeolite (ZFA) from coal fly ash and modified it by chitosan. Results obtained by Xie et al (2013) showed that the chitosan modified zeolite enhanced the adsorption performance of zeolite ZFA. Ngah et al (2012) did a study on chitosan-zeolite composite as an adsorbent to remove copper from aqueous solution.
Work has been done where MOFs (ZIFs in particular) have been impregnated with chitosan for different applications. Kang et al (2013) investigated ZIF-7/chitosan mixed –matrix membranes for separation of mixtures of water and ethanol in a pervaporation process (Kang et al, 2013). Casado-Coterillo et al (2015) successfully synthesized and characterized MOF/ionic liquid/chitosan mixed-matrix membrane for separation of CO₂ and nitrogen (Casado-Coterillo et al, 2015). The aforementioned authors used ZIF-8 as MOF. Chitosan has high potential for the removal of metal ion; this is because chitosan has amine and hydroxyl groups that serve as active sites for metal ions (Ngah et al, 2012). Therefore chitosan and MOFs have potential to be used as composite adsorbent.

Sneddon et al, (2015) reported on a family of chitosan/mesoporous silica composite materials with a simple deposition method for CO₂ capture. The materials had a maximum CO₂ adsorption capacity of 0.98 mmol/g at a temperature of 25°C and pressure of 1 atm and they could be regenerated at a low temperature of 75°C. Chitosan/mesoporous silica retained about 85% capacity after 4 cycles.

CO₂ adsorption can take place on the free amine groups of glucosamine found in chitosan through cooperative adsorption of one CO₂ molecule with two adjacent amine group the same way to amine based adsorbents (Sneddon et al, 2015). Chitin from which chitosan is produced is a major food waste from the sea food industry (Sneddon et al, 2015). This provides an opportunity for mass scale production of chitosan for CO₂ capture (Sneddon et al, 2015). By doing so, chitosan would be used to tackle another environmental problem.

As far as could be ascertained, no work has been reported on the study where chitosan is impregnated on MOFs and applied for CO₂ capture. Therefore this work investigated impregnation of chitosan on MOFs (SOD-ZMOF in particular). The presence of amine groups on chitosan can enhance the adsorption capacity of SOD-ZMOF as amines are basic while CO₂ is acidic. Amine is known to react easily with carbon dioxide to form carbamates.

*Factors affecting adsorption process*

They are several factors that influence adsorption of CO₂. Adsorbents are first characterized by surface properties such as polarity and surface area. During the adsorption process, there are several factors that affect adsorption. These are factors such as temperature, pressure, nature of adsorbate and concentration of adsorbate.
Generally temperature increase results in decrease in adsorption since adsorption is an exothermic process (Dhawan & Dhawan, 2011). At constant temperature, the rate adsorption of a gas increases with increase in pressure (Dhawan & Dhawan, 2011). At the same temperature, the degree at which different gases are adsorbed by the same adsorbent is not the same. Nature of adsorbent also affects adsorption. An adsorbent with a rough surface will have greater number of pores than an adsorbent with a smooth surface. Thus a rough surface adsorbent can adsorb greater number of molecules than a smooth surface adsorbent (Dhawan & Dhawan, 2011). Extent at which adsorption occurs is affected by surface area of adsorbent. Greater the surface area of adsorbent means the greater the extent of adsorption. Specific surface area is the surface area of adsorption per gram of adsorbent (Dhawan & Dhawan, 2011).

2.5. **Summary**

CCS allows the continuous used of coal for energy generation while reducing CO$_2$ being released to the atmosphere. Post-combustion capture is the most advantageous technology as it is easy to retrofit in power plants. Adsorption is the best capture method because it requires less energy as compared to other capture methods.

From the previous sections it can be observed that much work has been reported since MOFs were developed over the last decade. From literature a lot of investigation of CO$_2$ capture using MOFs as adsorbents has been reported. Researchers have also modified MOFs by impregnation and grafting with liquids like amines and ionic liquid. Chen et al (2011) developed SOD-ZMOFs and investigated these materials for CO$_2$ capture. The aforementioned authors also grafted the SOD-ZMOFs with an amine group and the results from their work showed that the SOD-ZMOF and modified SOD-ZMOF are excellent adsorbents for CO$_2$ capture. Gupta et al (2012) did a simulation study on impregnating ionic liquid ([SCN] [BIMM]) on rho-ZMOF and results did show that the material had a good CO$_2$ adsorption capacity.

As far as could be ascertained, no work has been reported in capturing CO$_2$ using SOD-ZMOF-chitosan composite. Chitosan has been applied as a composite with other materials in industries such water treatment as explained above. Not much work has been reported in using chitosan composite materials for CO$_2$ capture. Past studies have shown the possibility of incorporating chitosan in zeolite materials for removal of pollutants in water. In the same manner, the presence of functional groups such as (-NH$_2$-) and (OH) in chitosan may be
useful in making ZMOF-chitosan composite adsorbent for CO₂ capture. The presence of amine group in chitosan can promote the adsorption of CO₂. On this basis, this study aims to design a composite adsorbent for CO₂ capture by incorporating chitosan on SOD-ZMOFs.

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CHAPTER 3: EXPERIMENTAL PROCEDURE

This chapter reports on the materials and procedure employed in the synthesis, characterization and performance evaluation of SOD-ZMOF-chitosan adsorbent. Section 3.1 reports on the materials used Section 3.2 reports on the synthesis of the adsorbent, Section 3.3 reports on the characterisation and lastly Section 3.4 describes how the synthesized adsorbent was evaluated for CO₂ capture. Figure 3.1 depicts an overview of the experimental methodology used in this work.

(a) Synthesis

Start → Adsorbent synthesis → Chitosan → sod-ZMOF → sod-ZMOF chitosan

(b) Adsorbent characterisation

Characterisation → XRD - crystallinity → FTIR – Surface chemistry → BET – Surface area, pore volume → Was adsorbent successfully synthesized?

---

(c) Performance evaluations

Performance Evaluation of sod-ZMOF chitosan → TGA (100% CO₂) Varying Temperature and Gas Flow rate → Does chitosan impregnation increase sod-ZMOF adsorption capacity?

End → YES → Performance Evaluation of all 3 Adsorbents → TGA (100% CO₂) → Varying Temperature and flow rate → Packed Bed Column (15% CO₂) Varying Temperature and Gas Flow rate → End

Figure 3.1: Summary of research methodology
3.1. Materials and Adsorption equipment

3.1.1. Materials
The chemicals used in the study: 98 % 4, 5 Imidazoledicarboxylic acid, 99 % imidazole, 99.99% indium (III) nitrate hydrate, hydrochloric acid, 99.8 % N, N-dimethylformamide (DMF), 70% sodium hydroxide (NaOH), 70 % nitric acid, 99.8 % acetonitrile, 99.8% methanol and 99.98 % acetic acid were all purchased from Sigma Aldrich, South Africa. The chitin was obtained from the shell of crabs (usually a waste material from restaurants). The gas mixture, 15%-85% CO₂-N₂, 100% CO₂ and nitrogen baseline were obtained from Afrox, South Africa.

3.1.2. Description of Adsorption equipment
Adsorption experiments were performed using a thermogravimetric analyser (TGA) of type TA-Q600 as well as adsorption equipment which contain a packed-bed adsorption column (Figure 3.2). Both TGA and adsorption equipment are connected to a gas flow panel and the flowrate of the influent gas was controlled using a mass flow controller. Adsorption is shown through weight changes of the adsorbent for the TGA, while for the adsorption equipment adsorption is shown through changes in concentration of effluent gas stream.

3.2. Synthesis of SOD-ZMOF-chitosan composite

3.2.1. Synthesis of SOD-ZMOF
The method used to synthesize SOD-ZMOF in this study was adapted from the work reported elsewhere (Chen et al, 2011). About 0.84 g 4.5-imidazoledicarboxylic acid, 0.6 g indium (III) nitrate hydrate (In(NO₃)₃.2H₂O), 60 mL N, N-dimethylformamide (DMF), 20 mL acetonitrile (CH₃CN), 0.82 g imidazole in 8 mL DMF and 1.8 mL nitric acid (HNO₃) in 12 mL DMF were added into a 100 mL flask. The solution was mixed thoroughly until a clear solution was obtained. The solution was heated up to 85°C under reflux for 12 h. after 12 h, the temperature was increased to 105°C and continued heating for 23 hours. Polyhedral crystals formed where collected by filtration; washed with methanol to remove any DMF from the pores and surface and then dried in an oven at 100 °C for 2 h. The dried poly crystals obtained were SOD-ZMOF.

3.2.2. Production of chitosan
The crabs flesh was removed, the exoskeletons thoroughly washed and sundry. The dried exoskeletons were then chopped into smaller sizes, pulverized to a particle size of < 74 nm.
For preparation of chitosan, chitin was sieved and subjected to demineralization, deproteinization and decolonization.

Chitin was added to 10% (v/v) hydrochloric acid (HCl) with a solvent to solid ratio of 1:10. The reaction was carried out at 65 °C for 2 h with continuous stirring, after which the obtained material was filtered and washed with distilled water until filtrate pH was neutral. The resulting sample was dried in an oven at 50 °C for 24 h.

The demineralized chitin was added to 4% (w/v) Sodium hydroxide (NaOH) with a solvent to solid ratio of 1:10 and heated at 65 °C for two h with continuous stirring. The resultant product was then filtered and washed with distilled water to a neutral pH. The sample was dried in an oven at 50 °C for 24 h.

About 50 g of Deproteinized chitin was added to 50% (w/v) of Sodium hydroxide (NaOH) at 90 °C for 5 h with continuous stirring. The resultant product was filtered, washed with distilled water to a neutral pH and dried in an oven at 50 °C for 24 h.

3.2.3. Development of SOD-ZMOF-chitosan composite adsorbent

The procedure used for impregnation of chitosan was adapted from the work reported elsewhere (Sun et al., 2008). Chitosan was dissolved in 2 wt. % acetic acid and stirred at 80 °C for 1 h to obtain 2 wt. % chitosan solution. 1 g of SOD-ZMOF was added into the solution under stirring for 1 h. The suspension mixture was filtered and the obtained product dried in an oven at 50 °C for about 2 h.

3.3. Characterisation techniques

Characterization of SOD-ZMOF-chitosan was done before and after chitosan impregnation. It is important to understand the changes in SOD-ZMOF after chitosan was impregnated. X-ray diffraction (XRD) was done in order to determine the crystallinity of the synthesized adsorbent. The XRD patterns in this study were obtained using a cobalt (CoKα) radiation with wavelength (λ) of 1.79 Å. Fourier Transform Infrared Spectroscopy (FTIR) was used to check the surface chemistry of the synthesized adsorbents. N2 physisorption at 77 K was carried out to determine the BET surface area, pore volume and the pore size of the synthesized adsorbent.
3.4. Performance evaluation

3.4.1. TGA performance evaluation
Thermal galvanic analysis was first used to evaluate the adsorption capacity of SOD-ZMOF, chitosan and SOD-ZMOF-chitosan at an adsorption temperature of 25°C, pressure of 1 bar and flowrate of 60 ml/min. 100 % CO₂ was used to evaluate the aforementioned adsorbents. About 11 mg of adsorbent was used. Only 11 mg was used because this was the maximum mass that could be loaded on the TGA. First nitrogen is passed through the adsorbent at a sweeping temperature of 110 °C for 30 minutes in order to remove any impurities in the adsorbent. At constant pressure, a traditional method was used to investigate the effect of adsorption temperature and influent gas flowrate at a temperature range and gas flowrate range listed in Table 3.1. Amount of CO₂ adsorbed during the experiment was obtained using the CO₂ concentration before and after adsorption:

\[
\% \text{ CO}_2 \text{ adsorbed} = \frac{\text{Weight of adsorbent after adsorption} - \text{Weight of adsorbent before adsorption}}{\text{Weight of adsorbent before adsorption}}
\]

Table 3.1: Operating conditions investigated

<table>
<thead>
<tr>
<th>Operating Conditions</th>
<th>Value (range)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption temperature range</td>
<td>25 -85 °C</td>
</tr>
<tr>
<td>Influent gas flowrate range</td>
<td>15- 90 ml/min</td>
</tr>
<tr>
<td>Operating pressure</td>
<td>1 bar</td>
</tr>
</tbody>
</table>

3.4.2. Packed-bed column evaluation
Adsorption set-up depleted in Figure 3.2 was used to evaluate the CO₂ adsorption performance of the synthesized SOD-ZMOF-chitosan. The set-up consists of a packed-bed column connected to a CO₂ detector in order to read the CO₂ concentration before, during and after adsorption. About 0.05 g of the adsorbent was packed in the column. The sample in the column was then heated from room temperature to 110°C under the continuous flow of nitrogen through the sample and held for another 30 minutes at 110°C for sweeping impurities such as moisture from the adsorbent. Then the temperature was dropped to the 25 °C. A influent gas mixture of about 15% CO₂ (balance being nitrogen) at a flowrate of 25 ml/min and a pressure of 1 bar was passed through the sample for about 1 h., which contains
about 15% CO\textsubscript{2}. Amount of CO\textsubscript{2} adsorbed during the experiment was obtained using CO\textsubscript{2} mass balance as a mathematical relationship below Equation 3.2:

\[
q = \frac{P \times M_r}{R \times T \times m_{\text{adsorbent}}} \left( Q(y_i - y_f) \right) \times t
\]  

Where q is the amount of CO\textsubscript{2} adsorbed in mol/g adsorbent (to express the amount in mg CO\textsubscript{2}/g adsorbent, q was multiplied by the molar mass of CO\textsubscript{2} (M\textsubscript{r})), y\textsubscript{i} and y\textsubscript{f} is the mole fractions of CO\textsubscript{2} in the influent and effluent gas streams, respectively, Q is the volumetric flowrate of the feed stream. P and T are the adsorption pressure and temperature, respectively. R is the universal gas constant; m\text{adsorbent} is the mass of the adsorbent, M\textsubscript{r} is the molar mass of CO\textsubscript{2}, and t is the adsorption time. The aforementioned procedure was repeated at adsorption temperatures of 40 °C, and 55 °C with constant influent gas flowrate and then repeated for varying influent gas flowrate keeping adsorption temperature and pressure constant at 25 °C and at 1 bar, respectively. The gas mixture employed in the study was used to mimic the composition of flue gas expected from a typical coal-fired power plant. A packed-bed column with diameter of 4 mm, bed height of 12 mm and operated at a pressure of 1 bar was utilized in this work.

![Figure 3.2: Process flow diagram of the adsorption set-up](image-url)
References


CHAPTER 4: SYNTHESIS AND CHARACTERISATION OF SOD-ZMOF-CHITOSAN COMPOSITE ADSORBENT

4.1. Introduction
The first objective of this work was to synthesise SOD-ZMOF and compare results with literature. The first part of the second objective was to impregnate chitosan on SOD-ZMOF. This chapter reports on these objectives. After synthesis it is important to characterize the sample for comparison with literature as well as to identify the properties of the synthesized material. This section discusses the characterisation results of SOD-ZMOF, chitosan and SOD-ZMOF-Chitosan. Characterisation techniques used in this study were XRD for phase identification and crystallinity, FTIR for surface chemistry and N₂ physisorption at 77 K for surface area and pore volume.

4.2. Experimental

4.2.1. Synthesis
SOD-ZMOF and SOD-ZMOF-chitosan were synthesized using the methodology discussed in chapter 3. To recap, SOD-ZMOF was first synthesized using the method adapted from Chen et al (2011). Chitosan was then derived from chitin of crabs purchased from a beach in Lagos, Nigeria. Finally chitosan was impregnated on the synthesised SOD-ZMOF using a method adapted from Sun et al (2008).

4.2.2. Characterisation techniques for SOD-ZMOF and SOD-ZMOF-chitosan
Figure 4.1 depicts an overview of the characterisation techniques used in this study as well as what they were used for. After synthesis, SOD-ZMOF and SOD-ZMOF-chitosan were characterized. First, SOD-ZMOF characterisation results were compared to those obtained from literature (Chen et al, 2011). This was done to confirm if the properties of the synthesized SOD-ZMOF was similar to that reported in literature. After it was confirmed that the synthesized material was SOD-ZMOF, SOD-ZMOF and SOD-ZMOF chitosan were compared in order to observe the changes in properties before and after chitosan impregnation.
4.3. Results and Discussion

4.3.1. Physicochemical characterization

Figure 4.2 depicts the XRD pattern of SOD-ZMOF before and after chitosan impregnation. XRD was characterized to determine the crystallinity of SOD-ZMOF is crystalline because MOFs are highly crystalline materials. XRD patterns of the SOD-ZMOF and chitosan-impregnated SOD-ZMOF were obtained using cobalt (CoKα) radiation with a wavelength of (λ) of 1.79Å. In literature, XRD patterns of SOD-ZMOF were obtained using copper radiation (CuKα) radiation with wavelength of 1.54 Å. In order to compare XRD patterns from this work with that from literature values obtained from CoKα radiation were corrected to expected values of CuKα (refer to Appendix A). The sharpness of the XRD peaks is important in identifying the crystallinity of SOD-ZMOF. The sharp peaks depicted in Figure 4.2 represent that the synthesized material is crystalline; this was expected as metal organic frameworks are highly crystalline materials. SOD-ZMOF showed a XRD pattern that is similar to that reported in literature (Chen et al., 2011; Calleja et al., 2010), confirming that SOD-ZMOF material were synthesised in this study.

The XRD pattern of chitosan impregnated SOD-ZMOF shows a comparable pattern to that of SOD-ZMOF indicating that the structure of SOD-ZMOF was still conserved after chitosan impregnation. At a 2-theta of about 30 degree, there is a drastic decrease in the intensity on
the XRD pattern of SOD-ZMOF-chitosan as compared to that of SOD-ZMOF. The decrease could be as a result of the impregnated chitosan in SOD-ZMOF. Thus chitosan was successfully impregnated on SOD-ZMOF to produce SOD-ZMOF-chitosan.

![XRD pattern of SOD-ZMOF before and after impregnation](image)

**Figure 4.2: XRD pattern of SOD-ZMOF before and after impregnation**

The FTIR spectra of SOD-ZMOF and SOD-ZMOF-chitosan are depicted in Figure 4.2. The organic linker in SOD-ZMOF is 4.5-Imidazolodicarboxylic acid and as such it is expected that SOD-ZMOF and this organic linker have similar functional groups. The functional groups present in 4.5-Imidazolodicarboxylic acid are amine (N-H), carboxylic acid (COOH), aromatics (C-C (in ring)), aromatic amine (CN) and (C=O). The FTIR analysis of SOD-ZMOF in Figure 4.3 shows the presence of COOH at a wavelength of 3178 cm\(^{-1}\), C-C (in ring) at a wavelength of 1476 cm\(^{-1}\), C-N at a wavelength of 1105 cm\(^{-1}\), N-H at a wavelength of 779 cm\(^{-1}\) and C=O at a wavelength of 1700 cm\(^{-1}\), which therefore confirms the successful synthesis of SOD-ZMOF. Table 4.1 contains defined explanation of the FTIR.

Figure 4.3 also shows FTIR spectrum for SOD-ZMOF-chitosan. The FTIR spectrum of SOD-ZMOF-chitosan showed functional groups similar to those found in SOD-ZMOF. However, there is a drastic decrease in the intensity of the COOH (carboxylic acid) band in the spectrum for SOD-ZMOF-chitosan as compared to that of SOD-ZMOF. When Chen *et al.* (2013) grafted SOD-ZMOF with ethylenediamine (EDA), the FTIR also showed a decrease in COOH band after grafting. Chen *et al.* speculated that the decrease in COOH band could be attributed to the transformation of the carboxylic acids to amide groups. In this work, the decrease in the COOH band could also be due to the impregnation of chitosan containing
amine which then confirms the presence of chitosan (amine group) in SOD-ZMOF chitosan. The expected functional group present in chitosan are amines (N-H), aliphatic amines (C-N) and alcohol (O-H) (Refer to Figure 2.13 for structure of chitosan). N-H is present at a wavelength of 876 cm\(^{-1}\), C-N is present at a wavelength of 1046 cm\(^{-1}\) and O-H is present at a wavelength of 3649 cm\(^{-1}\).

![Figure 4.3: FTIR spectra of SOD-ZMOF before and after chitosan impregnation](image)

<table>
<thead>
<tr>
<th>Wavelength (cm(^{-1}))</th>
<th>Functional group</th>
<th>Interpretation</th>
</tr>
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<tbody>
<tr>
<td>3640–3610</td>
<td>O-H</td>
<td>Alcohol</td>
</tr>
<tr>
<td>3300–2500</td>
<td>COOH</td>
<td>Carboxylic group</td>
</tr>
<tr>
<td>1710–1665</td>
<td>C=O</td>
<td>Unsaturated aldehydes</td>
</tr>
<tr>
<td>1500–1400</td>
<td>C-C (in ring)</td>
<td>aromatics</td>
</tr>
<tr>
<td>1250–1020</td>
<td>C-N</td>
<td>aromatic amines</td>
</tr>
<tr>
<td>910–665</td>
<td>N-H</td>
<td>1°, 2° amines</td>
</tr>
</tbody>
</table>
4.3.2. Surface area and pore volume

Nitrogen physisorption at 77 K was conducted on SOD-ZMOF before and after chitosan impregnation in order to determine the pore volume, pore size and BET surface area. Table 4.3 depicts a summary of the BET results obtained in this study. From work done in literature, SOD-ZMOF has a pore volume and BET surface area greater than the one obtained in this study.

Table 4.2: Comparison of textual properties

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOD-ZMOF</td>
<td>375</td>
<td>0.16</td>
<td></td>
<td>Chen et al (2011)</td>
</tr>
<tr>
<td>SOD-ZMOF</td>
<td>361</td>
<td>0.13</td>
<td></td>
<td>Calleja et al (2010)</td>
</tr>
<tr>
<td>SOD-ZMOF</td>
<td>52.40</td>
<td>0.0445</td>
<td>3.40</td>
<td>This work</td>
</tr>
<tr>
<td>Chitosan</td>
<td>17.1</td>
<td>0.119</td>
<td>27.0</td>
<td>This work</td>
</tr>
<tr>
<td>SOD-ZMOF–chitosan</td>
<td>0.527</td>
<td>0.0265</td>
<td>201.2</td>
<td>This work</td>
</tr>
</tbody>
</table>

In this study, SOD-ZMOF had a pore volume, pore size and BET surface which were much less than that obtained from the work of Chen et al. (2011) and Calleja et al (2010). In this work, the total volume of the reactant species solution was up-scaled compared to those of Chen et al (2011) and Calleja et al (2010). However, the reaction conditions were identical to that of Chen et al (2011) and Calleja et al (2010). Rubio-Martinez et al (2016) reported that synthesis of MOFs that proceed satisfactory in a small scale vessel may not always proceed well when scaled up using a bigger vessel at the identical process conditions as in a small vessel. According to Rubio-Martinez et al (2016), up-scaling of MOFs synthesis bring a challenge that affect product quality such as reduction of surface area. The aforementioned challenge was encountered in this work. McKinstry et al (2016) encountered a reduction in surface area per unit mass when the authors up-scaled the synthesis of MOF-5 by increasing the concentration of reactant species which caused interpenetration. Prasad & Suh (2012) observed a drastic reduction in surface area from 5290 m²/g to 1770 m²/g of a MOF with similar framework but differ only in degree of interpenetration. In MOFs synthesis, interpenetration is when the pore size of material is reduced without blockage of available
adsorptive sites (Jiang et al., 2013). Interpenetration is a phenomenon which negatively affects the porous nature of MOFs by reducing the size of pores (Jiang et al., 2013). Han et al. (2012) reported that interpenetration can sometimes create new CO$_2$ adsorption sites with high affinity at low pressures thus enhancing CO$_2$ uptake of material. However, this phenomenon decreases CO$_2$ uptake at high pressures of about 50 bar (Han et al., 2012).

One of the causes of interpenetration in MOFs is temperature and concentration conditions (Zhang et al., 2009; Prasad & Suh, 2012; Jiang et al., 2013). For this work, the amount of reactants species was increased while still maintaining the same molar ratio. A high volume of reactants species in a larger vessel (100 ml) was heated at the same temperature and same reaction time as a low volume of reactants in a small vessel (20 ml) reported in literature (Chen et al., 2011). Increasing the volume from 20 ml to 100 ml could have resulted in materials such as Structure Direction Agent (SDA) and solvent being occluded in the SOD-ZMOF structure thus occupying the available pores resulting to interpenetration.

In an attempt to remove the occluded material from the SOD-ZMOF, drying temperature was increased from 100°C to 150°C. However this resulted in the structure of SOD-ZMOF being affected as the FTIR spectra in Figure 4.4 illustrates the FTIR spectra of the SOD-ZMOF where drying occurred at 100°C and 150°C are different. The carboxylic acid at a wavelength of about 3116 cm$^{-1}$ completely disappeared for the SOD-ZMOF that was dried at 150°C as compared to the one dried at 100°C. This shows that the structure of SOD-ZMOF was affected. This is expected as metal organic frameworks are unstable at high temperatures (Lee & Park, 2015).

![Figure 4.4: FTIR spectra of SOD-ZMOF dried at different temperatures](image-url)

Heated at 150 degree celcius

Heated at 100 degree celcius

Wavelength (cm$^{-1}$)
In addition, impregnation of chitosan on SOD-ZMOF resulted in a decrease in surface area and pore volume. The decrease in surface area and pore volume is expected as chitosan impregnated occupies the surface area and pore volume in SOD-ZMOF. The decrease in surface area and pore volume is a significant indication of the successful impregnation of chitosan. Chen et al (2011) also observed a decrease in surface area and pore volume when they grafted amine onto SOD-ZMOF.

4.4. Summary
The first objective of this study was to synthesize SOD-ZMOF and compare results with literature and the second objective to impregnate chitosan on SOD-ZMOF. SOD-ZMOF was successfully synthesized and their physiochemical properties with textual properties with the exception of BET are comparable with those reported literature. BET analysis results showed a reduction in surface area compared to that reported by Chen et al (2011). The decrease in surface area could be as a result of interpenetration. After chitosan impregnation there was a decrease in surface area per unit mass. SOD-ZMOF crystal structure was still maintained after chitosan impregnation. Thus chitosan was successfully impregnated onto SOD-ZMOF.

References


CHAPTER 5: PERFORMANCE EVALUATION OF SOD-ZMOF-CHITOSAN COMPOSITE ADSORBENT FOR CO₂ CAPTURE

5.1. Introduction
After characterising the synthesised adsorbents (SOD-ZMOF, SOD-ZMOF-chitosan and chitosan), they were evaluated for CO₂ capture. The second objective of this work was to study the performance of SOD-ZMOF, chitosan and SOD-ZMOF-chitosan during CO₂ capture. Performance evaluation is significant as it shows if the synthesized adsorbent can capture CO₂. This Chapter reports on results of the evaluation of SOD-ZMOF, chitosan and SOD-ZMOF-chitosan adsorbents for CO₂ adsorption. SOD-ZMOF was impregnated with chitosan to produce SOD-ZMOF-chitosan composite. Thermal gravimetric analysis and packed-bed column were used to evaluate the performance of the aforementioned adsorbents. CO₂ adsorption using 100% CO₂ with TGA was carried out to evaluate if the synthesised adsorbents can adsorb CO₂ without the influence of impurities like N₂. Then the CO₂ adsorption was carried out using a gas mixture containing 15% CO₂ and 85% N₂ in a packed bed column. This was done because flue gas from post-combustion capture has a maximum concentration of 15% CO₂ with N₂ as one of the impurities.

5.2. Experimental
Experimental procedure described in section 3.2 was used. SOD-ZMOF, chitosan and SOD-ZMOF-chitosan were all evaluated for CO₂ adsorption using the TGA as well as the adsorption equipment depicted in Figure 3.1. The aforementioned adsorbents were investigated at 25°C, pressure of 1 bar and influent gas flowrate of 25 ml/min for packed-bed column and 25°C, 1 bar and 30 ml/min for the TGA.

5.3. Results and discussion
5.3.1. TGA performance evaluation
Adsorption of CO₂ using SOD-ZMOF, chitosan and SOD-ZMOF-chitosan was first investigated using the TGA as it is the equipment mostly used in literature. Figure 5.1 depicts a profile of how adsorption occurs when a TGA is used (Refer to appendix C for the TGA profile of individual samples). The TGA measures the weight percentage of the adsorbent as a function of time. First when nitrogen is passed through the adsorbent for sweeping, the weight percentage of the adsorbent decreases with adsorption time. This indicates that
something (in this case, impurities) is being removed from the adsorbents. When CO$_2$ is passed through the adsorbent the weight percentage increases indicating that CO$_2$ is attaching on the surface of the adsorbent. The weight percentage of the adsorbent of CO$_2$ increases until adsorbent is saturated and adsorption is complete. When adsorption is complete the weight percentage of the adsorbent remains constant with further increase in time. The reason for this is that the gas will just be passing over the adsorbent because the pores of the adsorbent are saturated.

![Figure 5.1: Profile of TGA adsorption profile](image)

At an adsorption temperature of 25°C, pressure of 1 bar and influent gas flowrate of 30 ml/min, SOD-ZMOF-chitosan displayed the highest adsorption capacity followed by SOD-ZMOF, and chitosan displayed the lowest adsorption capacity (refer to Figure 5.2). This is expected as impregnated chitosan contains amine group. Amines have high affinity for CO$_2$ through acid base interaction between the slightly acid CO$_2$ and basic amines. In addition, the SOD-ZMOF provided a larger surface area for the adsorption of CO$_2$ in the chitosan impregnated SOD-ZMOF. There was a 39% increase in CO$_2$ adsorption capacity of SOD-ZMOF after chitosan impregnation.
5.3.2. CO$_2$ adsorption capacity in packed-bed column

After it was determined that synthesized adsorbents can adsorb 100% CO$_2$, CO$_2$ adsorption performance of SOD-ZMOF, chitosan and SOD-ZMOF-chitosan was then evaluated using the adsorption set-up depicted in Figure 3.2. The performance evaluation of the adsorbents was determined using a gas mixture containing CO$_2$ (15%) and N$_2$ (85%). Unlike with TGA, the packed-bed column is connected to a CO$_2$ gas analyser which records the concentration of CO$_2$ in the effluent gas mixture and not the weight percentage of the adsorbent. During the indication of the CO$_2$ adsorption by the gas analyser, the CO$_2$ concentration reading in the effluent gas stream starts to decrease with adsorption time indicating that some of the CO$_2$ was adsorbed onto the adsorbent from the influent stream. After a certain time, the gas analyser displayed an increase in the CO$_2$ concentration and continued to increase until it reached the initial concentration in the influent stream, indicating the completeness of the adsorption process. Figure 5.3 depicts the CO$_2$ concentration profile of the adsorption process as obtained from the CO$_2$ gas analyser.
SOD-ZMOF-chitosan, chitosan and SOD-ZMOF were evaluated for CO$_2$ adsorption using the adsorption set-up in Figure 3.1. Operating conditions were temperature of 25°C, pressure of 1 bar and influent gas flowrate of 25 ml/min. After chitosan was impregnated on SOD-ZMOF, there was a huge reduction in surface area. However, as depicted in Figures 5.2 and 5.4, the CO$_2$ adsorption capacity increased after chitosan impregnation. The increase in the adsorption capacity after chitosan impregnation could be attributed to the role played by impregnated amine present in chitosan on the SOD-ZMOF. The interaction between slightly acidic CO$_2$ and slightly basic impregnated amines in chitosan facilitates CO$_2$ adsorption through formation of carbamate covalent bonds. With SOD-ZMOF adsorption mechanism is physisorption. When CO$_2$ comes in contact with SOD-ZMOF, CO$_2$ molecules attaches on the available adsorption sites on the surface of SOD-ZMOF. For SOD-ZMOF-chitosan, adsorption mechanism is chemisorption where CO$_2$ and amine present in chitosan form a carbamate covalent bond. When Chen et al (2013) impregnated EDA on SOD-ZMOF, its adsorption capacity increased by 30% and the authors speculated that it was due to the introduction of amine groups which interacts specifically with CO$_2$ through formation of carbamate-like complexes (Chen et al, 2013). In this study, similar observation occurred and
16% increase in CO₂ adsorption capacity was obtained for the SOD-ZMOF-chitosan adsorbent.

Both the TGA and packed-bed column showed an increase in adsorption capacity of SOD-ZMOF after chitosan impregnation. However the values of the adsorption capacity obtained using the packed-bed column is higher than those obtained using TGA (Figure 5.2). This could be because the TGA provides less contact between the gas and the adsorbent as compared to the packed-bed column. In a TGA, the gas flows on top of the adsorbent, while in a packed-bed column the gas flows through the bed (refer to Figure 5.5). It is speculated that, for a TGA, the gas only has contact with the top layer of the adsorbent since the gas flows horizontally over the top whereas with the packed-bed column the gas flows vertically through the adsorbent (refer Figure 5.5). As a result, with the packed column, there is greater mass transfer between the gas and the adsorbent because the gas flows directly through the adsorbent. The other reason for the huge difference in adsorption capacity could be the fact that with the TGA the mass of the adsorbent used was 11 mg as the TGA was limited to this mass only whereas 50 mg of adsorbent was used for the packed-bed column and it’s almost 4 times greater than the amount in the TGA. Extremely higher adsorption capacity obtained using the packed-bed column could be attributed to the systematic errors from the set-up. However it should be emphasized that the experiments were repeated severally for repeatability and accuracy.

Figure 5.4: CO₂ adsorption capacity of MOFs and chitosan using packed-bed column
5.4. Results compared with literature

CO₂ adsorption performance of SOD-ZMOF-chitosan was compared with other adsorbents in literature. It should be noted that conditions and type of equipment at which adsorption was used for adsorption influence the adsorption capacity of adsorbents as discussed in detail in Chapter 2. Table 5.1 depicts different type of adsorbents that were tested for CO₂ capture at different conditions and using different adsorption methods as obtained from literature.
Table 5.1: Comparison of adsorbents and adsorption methods

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity (mg CO₂/ g adsorbent)</th>
<th>Operating conditions/Equipment</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-100</td>
<td>792</td>
<td>50 bar, 31 °C/ Volumetric adsorption unit</td>
<td>Llewellyn et al (2008)</td>
</tr>
<tr>
<td>MOF-177</td>
<td>1474</td>
<td>35 bar, room temperature/ Volumetric adsorption unit</td>
<td>Millward &amp; Yaghi (2005)</td>
</tr>
<tr>
<td>PAA</td>
<td>44</td>
<td>1 bar, 40 °C/ TGA</td>
<td>Chitsiga et al (2016)</td>
</tr>
<tr>
<td>ZIF</td>
<td>30</td>
<td>1 bar, 25 °C/ TGA and BEL adsorption unit</td>
<td>Chen et al (2011)</td>
</tr>
</tbody>
</table>

60 mg of Mg based MOF-74 was evaluated for CO₂ capture using a volumetric adsorption unit. MIL-100 and MIL-101 were evaluated for CO₂ capture using a volumetric (1 g of
adsorbent), gravimetric (0.5 g of adsorbent) and Microcalorimetry (0.3 g of adsorbent) adsorption unit. 15 mg Cu-BTC and zeolite 13X were evaluated for CO$_2$ adsorption using integrated gravimetric sorption analyser (IGA unit). ED-SOD-ZMOF, SOD-ZMOF ZIF and PAA were evaluated using a TGA, thus their low adsorption capacities compared to other adsorbents in table 5.1. In this work, SOD-ZMOF-chitosan was evaluated using a TGA and a packed-bed column.

Most of the adsorbents in Table 5.1 including, MIL-100, MIL-101, PAA, SOD-ZMOF-ED-SOD-ZMOF, ZIF and Mg-based MOF-74 were evaluated using pure CO$_2$. In these work 100% CO$_2$ was used for adsorption tests using the TGA and 15% CO$_2$ was used for adsorption tests using the packed-bed column. From Table 5.1, MIL-101 showed the highest adsorption capacity, but this at relatively high pressure compared to the conditions at which other adsorbents in table 5.1 were subjected to during adsorption. The reported adsorption capacity of MIL-101 is almost 44% greater than that of SOD-ZMOF-chitosan, however this at different operating conditions and when using different adsorption equipment. SOD-ZMOF-chitosan is comparative with other adsorbents reported in literature.

5.5. Summary

SOD-ZMOF-chitosan composite displayed the highest adsorption capacity followed by SOD-ZMOF and chitosan had the lowest adsorption capacity. SOD-ZMOF-chitosan showed higher adsorption capacity of 781 and 23 mg CO$_2$/g adsorbent using the packed-bed column and TGA respectively. Impregnation of chitosan on SOD-ZMOF improved CO$_2$ adsorption capacity by 16 % for packed-bed column and 39% in a TGA. Adsorption capacity is higher when a packed-bed column was used as compared to when a TGA was used due to enhanced direct contact between the gas and adsorbent. SOD-ZMOF-chitosan is comparative with other adsorbents reviewed in literature.

References


CHAPTER 6: INFLUENCE OF OPERATING CONDITIONS ON CO₂ ADSORPTION CAPACITY OF SOD-ZMOF COMPOSITE

6.1. Introduction
Having understood the CO₂ adsorption performance of the SOD-ZMOF-chitosan as reported in the previous chapter, the adsorbent was then evaluated at different operating conditions to evaluate the effect of adsorption conditions on the CO₂ adsorption capacity of the adsorbent. It is important to know how the behaviour of the synthesized adsorbent changes at different operating conditions. The traditional method approach was one variable is varied at a time and the others kept constant was used. Results of the third objective of this study are hereby presented in this chapter.

6.2. Experimental
Experimental procedure described in Chapter 3 was used. However, adsorption temperature as well as gas mixture flowrate were varied in order to investigate the effect of these operating conditions on the CO₂ adsorption capacity of SOD-ZMOF-chitosan. The temperatures and gas flowrate investigated for the packed-bed column and the TGA are depicted in Table 6.1.
Table 6.1: Investigated operating conditions for packed bed and TGA

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature (°C)</th>
<th>Pressure (bar)</th>
<th>Gas flowrate (ml/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>55</td>
<td>1</td>
<td>25</td>
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<tr>
<td>4</td>
<td>25</td>
<td>1</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>1</td>
<td>70</td>
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<td>60</td>
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<tr>
<td>7</td>
<td>40</td>
<td>1</td>
<td>60</td>
</tr>
<tr>
<td>8</td>
<td>55</td>
<td>1</td>
<td>60</td>
</tr>
<tr>
<td>9</td>
<td>70</td>
<td>1</td>
<td>60</td>
</tr>
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<td>10</td>
<td>85</td>
<td>1</td>
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<td>1</td>
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</tr>
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<td>13</td>
<td>25</td>
<td>1</td>
<td>75</td>
</tr>
<tr>
<td>14</td>
<td>25</td>
<td>1</td>
<td>90</td>
</tr>
</tbody>
</table>

6.3. Results and discussion

6.3.1. CO₂ adsorption capacity behaviour with time in TGA and packed-bed column

Figure 6.1 depicts a function of adsorption capacity as a function of adsorption time for the TGA at different influent gas flowrates. As the gas attaches to the surface of the adsorbent, the weight of the adsorbent increases and it continues to increase until the available pores are filled up. Thus adsorption capacity increases drastically for the first 100 minutes. Adsorption capacity increases with adsorption time for all gas flowrates investigated until adsorbent was saturated. This is the point where adsorption is complete. This is expected because initially the adsorbent has free adsorption sites and as the gas passes through the adsorbent it fills these free adsorption sites until eventually with adsorption time the adsorption sites are filled. Once the adsorption sites on the adsorbent are filled, the adsorbent becomes saturated and the
gas just passes the adsorbent. Hence the adsorption capacity increased drastically initially and then the curve starts to become flat after about 150 minutes.

Figure 6.1: Adsorption capacity as a function of time (TGA)

Figure 6.2 depicts adsorption capacity as a function of adsorption time at different temperatures for the packed-bed column used in this study. The influent gas was passed through the packed-bed column for a total of 60 minutes while recording changes in CO₂ concentration of the effluent gas using the gas analyser. Adsorption capacity increased with adsorption time to a point and then starts to decrease. As the influent gas passed through the adsorbent, it fills the available adsorption sites of the adsorbent. Adsorption capacity continued to increase with adsorption time until all the available sites were filled. However once the available sites were filled up, the influent gas passed through the adsorbent with no adsorption occurring and this resulted in the decrease in the adsorption capacity because there was no more decrease in the CO₂ concentration of the effluent gas. Adsorption capacity decreased as the concentration reading of the effluent gas on the analyser increased to the initial concentration. At a temperature of 25°C, total adsorption time was about 44 minutes while at a temperature of 55°C, adsorption time was about 12 minutes. This shows that the kinetics of CO₂ adsorption was fast at higher adsorption temperature as compared to a low adsorption temperature. Such is expected because at a higher temperature, gas molecules have high kinetic energy than at low temperature. This means that at low temperature
molecules move slower through the adsorbent and can fill up all the adsorption sites, while at high temperature gas molecules move much faster and may not fill up all the adsorption sites.

Figure 6.2: Adsorption capacity as a function of time in the Packed-bed column

6.3.2. CO₂ adsorption behaviour with temperature in TGA and packed-bed column

Figures 6.3 and 6.4 depict the adsorption capacity of SOD-ZMOF-chitosan as a function of adsorption temperature for TGA and packed-bed column, respectively. For the TGA, at the lowest adsorption temperature of 25°C, adsorption capacity was 19 mg CO₂/ g adsorbent and reduced to 3 mg CO₂/ g adsorbent at a high temperature of 85°C. Adsorption capacity decreased from 781 mg CO₂/ g adsorbent at 25 °C to 314 mg CO₂/ g adsorbent at 55 °C for the packed-bed column (see Figure 6.2). For both the TGA and packed-bed column, CO₂ adsorption capacity of SOD-ZMOF-chitosan increased with decreasing adsorption temperature. This is expected as adsorption is an exothermic process (Yu et al., 2012). When influent CO₂ gas molecules come into contact with the adsorbent, the gas molecules are adsorbed by the adsorbent and heat is generated (that is heat of adsorption) (Mori & Yamada, 1994). Increasing adsorption temperature increases the kinetic energy of CO₂ gas molecules so at high adsorption temperatures CO₂ molecules have high kinetic energy thus they move faster and results in less adsorption time on the adsorbent surface, resulting thereby in low adsorption capacity at high adsorption temperature.
6.3.3. Effect of gas Flowrate on the CO₂ adsorption capacity of SOD-ZMOF-chitosan

SOD-ZMOF-chitosan was evaluated at different adsorption gas mixture flowrates using the TGA and packed-bed column depicted in Figure 3.2. The adsorption capacity of SOD-ZMOF-chitosan was evaluated at flowrates range from 25-70 ml/min and 30-90 ml/min for the packed-bed column and TGA, respectively, at constant temperature and pressure of 25°C.
and 1 bar. Figures 6.3 and 6.4 depict the CO₂ adsorption capacity of SOD-ZMOF-chitosan at these varying adsorption flowrates. At the lowest adsorption flowrate of 25 ml/min CO₂ adsorption capacity of SOD-ZMOF-chitosan was 781 mg CO₂/g adsorbent and at a high adsorption flowrate of 70 ml/min the adsorption capacity was just 194 mg CO₂/g adsorbent for the packed-bed column (see Figure 6.4). For the TGA, adsorption capacity of SOD-ZMOF-chitosan at a low adsorption flowrate of 30 ml/min was 23 mg CO₂/g adsorbent and at a high adsorption flowrate of 90 ml/min it was 20 mg CO₂/g adsorbent. In both the TGA and packed-bed column, adsorption capacity decreased with increase in adsorption flowrate. This could be because at low adsorption flowrates the CO₂ gas has high superficial velocity which results to less contact time between the CO₂ gas and the adsorbents compared to low adsorption flowrates. Superficial velocity is simply defined as the volumetric flowrate of the gas divided by the cross sectional area thus increase in adsorption gas flowrate results in increase in superficial velocity. Less contact time means there is adsorption time at the surface of the adsorbent resulting in the adsorption of fewer gas molecules at higher adsorption flowrates.

![Figure 6.5: Effect of gas flowrate on CO₂ adsorption capacity of SOD-ZMOF-chitosan using TGA](image-url)
In literature, several researchers usually use TGA to investigate CO₂ adsorption capacity of their adsorbents. In this study CO₂ was evaluated using the TGA and packed-bed column at different temperatures and gas flowrates. However similar trend regarding the influence of operating conditions on CO₂ adsorption capacity of the synthesised adsorbent was displayed with the TGA (see Figures 6.3-6.6). However the adsorption capacity obtained when a packed-bed column is higher than that obtained using a TGA in spite of using 100% CO₂ was used for the TGA and 15% CO₂/85% N₂ for the packed column. In the packed-bed column, there is greater mass transfer between the adsorbent and adsorbate (CO₂). Extremely higher adsorption capacity obtained using the packed-bed column could be attributed to the systematic errors from the set-up. However it should be emphasized that the experiments were repeated severally for repeatability and accuracy as explained in Chapter 5.

### 6.4. Summary

The final objective of this study was to investigate the effect of operating conditions on the CO₂ adsorption capacity of SOD-ZMOF-chitosan. Two operating conditions (adsorption temperature and flowrate) were investigated using the traditional approach. CO₂ adsorption capacity of SOD-ZMOF-chitosan increased with decrease in adsorption temperatures and flowrates. At the 25°C, CO₂ adsorption capacity was high as compared to the highest adsorption temperature investigated. CO₂ adsorption capacity was highest at low adsorption...
flowrates as compared to high adsorption flowrates for both the TGA and the packed-bed column. The highest adsorption capacity of 781 mg CO₂/ g adsorbent was obtained at 25°C, 1 bar and 25 ml/ min for the packed-bed column. With the TGA, the highest adsorption capacity was 23 mg CO₂/ g adsorbent at 25°C, 1 bar and 30 ml/ min. The significant difference in adsorption capacity when the packed-bed column and the TGA were used has been discussed in detail in chapter 5.

References


CHAPTER 7: CONCLUSIONS AND RECOMMENDATIONS

7.1. Conclusions
Climate change is a major challenge that the whole world is facing due to the increase in atmospheric concentration of GHG, especially CO$_2$. Increase in atmospheric concentrations of CO$_2$ has resulted in the capture of CO$_2$ from point sources such as coal fired power plants in an attempt to reduce the amount of CO$_2$ being released into the atmosphere. This is the first and most expensive stage of the process called CCS. CCS captures CO$_2$ from point sources and stores it in a way that it would not affect the atmosphere. The high cost of CO$_2$ capture methods has resulted in investment on research and development of capture technologies. Most common and mature capture technology is absorption; however this process has several drawbacks. Adsorption is a promising CO$_2$ capture alternative due to its ability to operate at medium temperature and pressure and being less energy intensive. For the aforementioned reasons, this work focused on synthesis and performance evaluation of SOD-ZMOF-chitosan for CO$_2$ capture through adsorption. The main aim of this work was to enhance the CO$_2$ adsorption capacity of SOD-ZMOF through impregnation of chitosan. The specific objectives were:

i) Can up-scaling synthesis protocol for producing SOD-ZMOF affect physicochemical properties of the synthesized crystals?
ii) Can SOD-ZMOF-chitosan composite adsorbent be synthesized successfully?
iii) What will be the performance of the adsorbent for post-combustion CO$_2$ capture?
iv) What will be the effect of operating variables on the CO$_2$ adsorption capacity of the material?

Up-scaling the synthesis protocol of SOD-ZMOF affected the surface area of the material as it had a low surface area compared to that reported in literature. However physiochemical properties (XRD and FTIR) of SOD-ZMOF were not affected. This observation confirms what has been reported in literature.

Effect of impregnation of chitosan on SOD-ZMOF on CO$_2$ capture by adsorption was investigated. First SOD-ZMOF was synthesized and chitosan was produced from chitin. Chitosan and SOD-ZMOF were then characterized using XRD, FTIR and BET. Then
chitosan was impregnated on SOD-ZMOF to produce SOD-ZMOF-chitosan which was also characterized using the aforementioned characterisation techniques.

XRD showed that SOD-ZMOF is a crystalline material and the XRD pattern obtained in this work was similar to that in literature (Chen et al., 2011). The XRD peaks of SOD-ZMOF-chitosan decreased but maintained a similar shape to that of just SOD-ZMOF meaning that chitosan was successfully impregnated and SOD-ZMOF maintained its crystallinity after chitosan impregnation.

FTIR spectra of SOD-ZMOF showed presence of functional groups that are also present in organic linker used to synthesize SOD-ZMOF meaning that SOD-ZMOF was successfully synthesized. FTIR spectra of SOD-ZMOF-chitosan showed a drastic decrease in the carboxylic acid band. It was speculated that this was due to the impregnation of chitosan which is a source of amine.

N₂ physisorption for BET surface area and pore volume was also conducted for SOD-ZMOF before and after chitosan impregnation. BET surface area, pore volume and pore size obtained in this work were lower than those obtained for SOD-ZMOF in literature and this could be due to interpenetration during up scaling the synthesis protocol in which total volume of the starting materials have been increased. Reports in literature show that up-scaling the synthesis of MOFs can lead to a reduction in surface area of the final product. In addition a drastic decrease in surface area, pore volume and pore size of SOD-ZMOF after chitosan impregnation was observed indicating a successful impregnation of chitosan on SOD-ZMOF.

SOD-ZMOF before and after chitosan impregnation were then evaluated for CO₂ capture using TGA and packed-bed column. First 100% CO₂ was used for CO₂ adsorption in a TGA and after determining that the synthesized adsorbent can capture pure CO₂, adsorbents were then evaluated in a packed-bed column using 15% CO₂. This was used in order to mimic flue gas conditions. In both TGA and packed-bed column, chitosan impregnated SOD-ZMOF had a high CO₂ adsorption capacity as compared to just SOD-ZMOF. This is due to the presence of amine groups on chitosan which have high affinity for CO₂. Packed-bed column displayed higher adsorption capacities than those of the TGA. This could be attributed to the enhanced direct contact between the gas and the adsorbent in the packed-bed column was used.
Effect of adsorption temperature as well as influent gas flowrate were investigated on the CO$_2$ adsorption capacity of SOD-ZMOF-chitosan. CO$_2$ adsorption capacity of SOD-ZMOF-chitosan increased with a decrease in temperature and inlet gas flowrate. This is expected as adsorption is an exothermic process, and an increase in flowrate increases the superficial velocity of the gas and thereby decreasing contact time between the gas and the adsorbent. Consequently, the maximum CO$_2$ adsorption capacity obtained at 25 °C, 1 bar and inlet CO$_2$ flowrate of 60 ml/min was 23 mg CO$_2$/ g adsorbent for adsorption using a TGA and a maximum of 781 mg CO$_2$/ g adsorbent for packed-bed column at 25 °C, 1 bar and inlet gas flowrate of 25 ml/min. After chitosan impregnation, CO$_2$ adsorption capacity of SOD-ZMOF increased by 39 % and 16 % using the TGA and the packed-bed column respectively. For industrial purposes, the packed-bed column can be easily up-scaled as compared to the TGA. In addition, packed-bed column has better mass transfer between gas and adsorbent than the TGA.

6.5. Recommendations

As far as could be ascertained, this is the first study on the scale-up study of the synthesis and evaluation of chitosan impregnated SOD-ZMOF for post-combustion CO$_2$ capture. It is recommended that future work should consider improving the synthesis procedure of the SOD-ZMOF-chitosan in order to minimize or avoid interpenetration of the solvent. The information provided in this study could pave the way for future investigation on up-scaling of the synthesis method of SOD-ZMOF for mass production of the material for CO$_2$ capture.

Synthesis of SOD-ZMOF-chitosan should be optimized by varying the concentration of chitosan to be impregnated on SOD-ZMOF. Traditional method was used to investigate the effect of operating variables such as adsorption temperature and influent flowrate. It is recommended that future work makes use of a statistical approach to investigate the effect of operating conditions on the CO$_2$ adsorption capacity of SOD-ZMOF-chitosan because the traditional approach always overlooks the interaction effects of these variables.

It is recommended that studies on desorption of SOD-ZMOF-chitosan are carried out. Desorption is an important process that recovers CO$_2$ from the adsorbent. Moisture is a challenge when it comes to post-combustion capture; therefore it is recommended that the effect of the presence of moisture in flue gas is investigated. Performance of the adsorbent for CO$_2$ capture should also be investigated using real flue from power plants.
Future work should look into optimization of the adsorption process using SOD-ZMOF-chitosan as adsorbents. It is important to identify conditions at which SOD-ZMOF-chitosan is more effective in order to optimize its CO₂ adsorption capacity.

Lastly, it was discovered in this study that the custom-built packed-bed adsorption column used for the evaluation of the performance of the up-scaled adsorbent might have overestimated the adsorption capacity due to systematic error from the set-up. In addition, analysis of the N₂ gas effluent from the adsorption column was not possible with the gas analyser attached to the set-up. It is hereby recommended that the trouble-shooting of the set-up should be carried out to identify the problem leading to the systematic error. In addition, the set-up should be provided with a gas analyser that could measure N₂ as well.
APPENDICES

Appendix A

For analysis XRD characterization was done using a cobalt XRD radiation with a wavelength of 1.78897 angstroms. Results obtained from this characterization had to be compared with that from literature. In literature, XRD characterization was done using copper radiation with a wavelength of 1.542 angstroms. For the sake of comparison, a ratio was calculated in order to normalize the two different wavelengths. Calculations were done as follow:

\[
\text{Ratio} = \frac{1.78897 \text{ angstroms}}{1.542 \text{ angstroms}} = 1.162
\]

This ratio was then used to normalize the wavelength of XRD cobalt data with copper wavelength by dividing cobalt raw XRD data by this ratio.
Appendix B: Adsorption runs and calculations results

B1. TGA

This shows the TGA adsorption data used to calculate the adsorption capacity

B.1.1. TGA Raw results

B.1.1.1 SOD-ZMOF and Chitosan

Figure B1: TGA for SOD-ZMOF at a flowrate of 30 ml/min, 1 bar and 25 °C
Figure B2: TGA for chitosan at a flowrate of 30 ml/min, 1 bar and 25 ℃

B.1.2. SOD-ZMOF-Chitosan

Figure B3: TGA for SOD-ZMOF-chitosan at a flowrate of 30 ml/min, 1 bar and 25 ℃
Figure B4: TGA for SOD-ZMOF-chitosan at a flow rate of 45 ml/min, 1 bar and 25 °C.

Figure B5: TGA for SOD-ZMOF-chitosan at a flow rate of 60 ml/min, 1 bar and 25 °C.
Figure B6: TGA for SOD-ZMOF-chitosan at a flowrate of 75 ml/min, 1 bar and 25 °C

Figure B7: TGA for SOD-ZMOF-chitosan at a flowrate of 75 ml/min, 1 bar and 25 °C
Figure B8: TGA for SOD-ZMOF-chitosan at a flowrate of 60 ml/min, 1 bar and 40 °C

Figure B9: TGA for SOD-ZMOF-chitosan at a flowrate of 60 ml/min, 1 bar and 55 °C
Figure B10: TGA for SOD-ZMOF-chitosan at a flowrate of 60 ml/min, 1 bar and 70 °C

Figure B11: TGA for SOD-ZMOF-chitosan at a flowrate of 60 ml/min, 1 bar and 85 °C
B1.2: Adsorption capacity as a function of time calculations

Table B1: TGA Adsorption capacity calculations for at 25°C, 1 bar and 30 ml/min

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Table B2: TGA Adsorption capacity calculations for at 25°C, 1 bar and 45 ml/min

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Table B3: TGA Adsorption capacity calculations for at 25°C, 1 bar and 60 ml/min

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Table B4: TGA Adsorption capacity calculations for at 25°C, 1 bar and 75 ml/min

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Table B5: TGA Adsorption capacity calculations for at 25°C, 1 bar and 90 ml/min

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Table B6: TGA Adsorption capacity calculations for at 25°C, 1 bar and 45 ml/min

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Table B8: TGA Adsorption capacity calculations for at 25°C, 1 bar and 75 ml/min

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Table B9: Packed-bed Adsorption capacity calculations for at 25°C, 1 bar and 25 ml/min

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Table B10: Packed-bed Adsorption capacity calculations for at 40°C, 1 bar and 25 ml/min

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Table B12: Packed-bed Adsorption capacity calculations for at 25°C, 1 bar and 70 ml/min

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Appendix C: Adsorption Equipment

C1. Packed-bed column

Figure D1 depicts the actual adsorption set-up of the packed-bed column used for CO2 adsorption evaluation in this work. The set-up is connected to nitrogen and 15% (balance being nitrogen) gas cylinders. The set-up is also connected to a CO2 gas analyser which detects the CO2 concentration before, during and after adsorption. It also consists of a flowmeter that reads the inlet CO2 flowrate in ml/min as it enters the system, a temperature and pressure control system used to set either temperature or pressure to desired values. An overview of this equipment is in figure 3.2
Figure C1: packed-bed column adsorption set-up

- Packed-bed column
- CO₂ gas analyser
- Temperature and pressure display
- Flowmeter
Appendix D: Published papers
Chitosan-impregnated sod-Metal Organic Frameworks (sod-ZMOF) for CO₂ capture: Synthesis and performance evaluation

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⁹School 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

A sodalite zeolite-like metal organic framework (sod-ZMOF) was impregnated with chitosan and evaluated for carbon dioxide (CO₂) capture. Sod-ZMOF before and after impregnation was characterized by x-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and N₂ physisorption. Chitosan impregnated sod-ZMOF (sod-ZMOF-chitosan) was then evaluated for CO₂ adsorption using a packed bed column using a gas mixture containing 15% CO₂ and 85% N₂. Sod-ZMOF-chitosan was evaluated at different temperatures and flow rates to understand the effect of these variables on the adsorption performance of the material. Sod-ZMOF-chitosan reached its best adsorption capacity of 978 mg CO₂/g adsorbent at a temperature of 25°C, flow rate of 25 ml/min and a pressure of 1 bar.

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Keywords: Adsorption; Chitosan; CO₂ capture; MOFs; Packed-bed column

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1. Introduction

Climate change is among one of the major challenges that the world is facing today. This is due to increase in greenhouse gases concentration, especially CO₂ in the atmosphere. Increase in atmospheric concentration of CO₂ has created an interest to reduce due to its effect on the environment. About 85% of the world's energy needs is produced from fossil fuel [1]. Fossil fuels will continue to be the primary source of energy for the world [2]. Fossil fuels are combusted to produce energy and CO₂ is an inevitable by-product. Removal of CO₂ from post combustion outlet streams is achieved through CO₂ capture. This is the first stage in a process called carbon capture and storage (CCS). CCS reduces the amount of CO₂ released into the atmosphere by capturing it from fossil fuel powered plants and storing it in a way that will not affect the atmosphere. However, the capture stage is challenging due to the high temperature and low partial pressure of CO₂ in the flue gas from the combustion outlet stream [3]. It is therefore essential to investigate capture technologies for CO₂ reduction. Various technologies including absorption, membrane separation and adsorption have been developed and are being actively investigated.

Absorption using synthetic liquid amines is the most mature and commercialized CO₂ capture technology. However, this technology possesses several drawbacks such as the large amount of energy required to regenerate the solvent and corrosive nature of the solvent [1, 4]. This calls for an efficient alternative for CO₂ capture. Adsorption using solid adsorbents exhibits many advantages in dealing with CO₂ post combustion capture [3]. Adsorption is the attachment of gas or solid molecules on a solid surface [5]. The aforementioned technology is less energy intensive as it can operate at moderate temperature and pressure [6]. Several kinds of solid materials such as carbon based materials, Silica based materials, zeolites and metal organic frameworks (MOFs) have been developed and investigated for CO₂ adsorption [1, 4].

MOFs are highly crystalline materials that have metal ions as centres and organic materials as linkers [7]. MOFs have been synthesized and investigated for CO₂ capture due to their high surface area, high porosity, open metal sites and desirable chemical properties [7]. There are different types of MOFs depending on choice of building blocks (metal ion, organic linker and structure directing agent). Zeolite-like metal organic frameworks (ZMOFs) are a member of the MOF family with topologies similar to that of zeolites [8]. ZMOFs with sodalite (sod) and rho topologies have been investigated for CO₂ capture by Chen et al. [8]. Chen et al. [8] reported adsorption capacity of 53 and 51 mg CO₂/g adsorbent for sod-ZMOF and rho-ZMOF respectively [8]. These ZMOFs showed relatively high CO₂ adsorption capacity and selectivity at ambient temperature and pressure as compared to other types of MOFs.

Additionally, the properties of MOFs can be enhanced by incorporating appropriate functional groups to the MOF structure through grafting, impregnation and ion exchange to improve its CO₂ adsorption capacity [9]. The Amine functional group is of particular interest for incorporating in solid adsorbents. This is because the interaction between basic modified amine active sites and acidic CO₂ enables adsorption by covalent bonding [4]. A major advantage of amine based adsorbents is that they require low heat of regeneration as compared to aqueous amines [4]. Chen et al. [10], grafted ethylenediamine (EDA) on sod-ZMOF to enhance its adsorption capacity and EDA grafted sod-ZMOF gave a 30% increase in adsorption capacity as compared to the ordinary sod-ZMOF [10].

In spite of the aforementioned advantages, amine-based adsorbents have drawbacks such as high cost and the environmental impact associated with synthetic amines; making it challenging for this adsorbents to be commercialized [4]. This calls for an alternative material that has strong affinity for CO₂ but which is also less expensive and has less impact on the environment. This work proposes chitosan as an alternative source of amine functional group to be impregnated on sod-ZMOF. Chitosan is a biocompatible, biodegradable and non-toxic polymer derived from chitin [11]. Chitin is a natural resource produced from crabs, insects and shrimps [11, 12]. Chitosan is a green material and is the second largest most abundant polymer on earth [11]. Properties of chitosan include high viscosity, high solubility in various media, ability to form films and capability to bind with various metal ions [11]. Due to its unique properties, chitosan has been applied in industries such as wastewater treatment, food industry, cosmetics, and agriculture and biomedical [11]. The presence of functionalities such as amine (-NH₂) and hydroxyl (-OH) in the chitosan molecules provides basis for interaction with other materials [13]. Therefore, of recent chitosan has been receiving great attention to be used as novel functional composite material [11]. Chitosan, being a biodegradable organic material with several amine groups depending on its degree of deacetylation, can be a
green material that could be used to substitute synthetic liquid amine chemical. Also, the final product; sod-ZMOF-chitosan would have very little environmental effect.

Against this background, the current work investigated the synthesis of sod-ZMOF-chitosan adsorbent through impregnation of chitosan onto sod-ZMOF as well as the evaluation of the adsorbent. Furthermore, the influence of temperature and gas flow rate on chitosan-impregnated sod-ZMOF CO₂ adsorption capacity was investigated. Chitosan was impregnated into sod-ZMOF in order to improve the chemical surface of sod-ZMOF so as to enhance the adsorption capacity of sod-ZMOF.

2. Experimental

2.1. Materials

The chemicals used in the study: 4,5-Imidazoledicarboxylic acid, imidazole, indium (III) nitrate hydrate, hydrochloric acid, sodium hydroxide and solvents; N,N-dimethylformamide (DMF), nitric acid, acetonitrile and acetic acid were all purchased from Sigma Aldrich South Africa. The chitin was obtained from the shell of crabs (usually a waste material from restaurants). The gas mixture, 15%-85% CO₂-N₂, and nitrogen baseline were obtained from Afrox, South Africa.

2.2. Synthesis of sod-ZMOF and sod-ZMOF-chitosan

2.2.1. Synthesis of Sod-ZMOF

The method used to synthesize sod-ZMOF in this study was adapted from the work reported by Chen et al [8]. About 2.1 g of 4,5-imidazoledicarboxylic acid, 1.5 g of indium (III) nitrate hydrate (In(NO₃)₃.2H₂O), 150 mL N,N-dimethylformamide (DMF), 50 mL acetonitrile (CH₃CN), 2.0 g imidazole in 20 mL DMF and 4.4 mL nitric acid (HNO₃) in 30 mL DMF were added into a 1000 mL flask. The solution was mixed thoroughly until a clear solution was obtained. The solution was heated up to 85 °C under reflux for 12 h. After 12 h, the temperature was increased to 105 °C and heating continued for 23 hours. Polyhedral crystals formed were collected by filtration; washed with methanol to remove any DMF from the pores and surface and then dried in an oven at 100 °C for 2 h. The dried white poly crystals obtained were sod-ZMOF.

2.2.2. Preparation of chitosan

The crab flesh was removed, and the exoskeletons were thoroughly washed and sun dried. The dried exoskeletons were then chopped into smaller sizes, pulverized to a particle size of < 74 nm. For preparation of chitosan, chitin was sieved and subjected to demineralization, deproteinization and decolonization. Chitin was added to 10% (v/v) hydrochloric acid (HCl) with a solvent to solid ratio of 1:10. The reaction was carried out at 65 °C for 2 h with continuous stirring, after which the obtained material was filtered and washed with distilled water until filtrate pH was neutral. The resulting sample was dried in an oven at 50 °C for 24 h. The demineralized chitin was added to 4% (w/v) sodium hydroxide (NaOH) with a solvent to solid ratio of 1:10 and heated at 65 °C for two h with continuous stirring. The resulting product was then filtered and washed with distilled water to a neutral pH. The sample was dried in an oven at 50 °C for 24 h. Thereafter, about 50 g of the deproteinized chitin was added to 50% (w/v) of sodium hydroxide (NaOH) at 90 °C for 5 h with continuous stirring. The resultant product was filtered, washed with distilled water to a neutral pH and dried in an oven at 50 °C for 24 h.

2.2.3. Impregnation of chitosan in sod-ZMOF

The procedure used for the impregnation of chitosan onto sod-ZMOF was adapted from the work reported by Sun et al. [14]. Chitosan was dissolved in 2 wt. % acetic acid solution and stirred at 80 °C for 1 h to obtain 2 wt. % chitosan
solution. 1 g of sod-ZMOF was added into the solution under stirring for 1 h. The suspension mixture was filtered and the obtained product dried in an oven at 50 °C for about 2 h.

2.3. Characterization

X-ray diffraction (XRD) analysis was carried out on the sample in order to check the purity and crystallinity of synthesized adsorbent. The XRD patterns in this study were obtained using a CoKα radiation with a wavelength (λ) of 1.79 Å. Fourier transform infrared spectroscopy (FTIR) analysis was carried out for surface chemistry of the synthesized adsorbent. N2 physisorption at 77 K was carried out to determine the BET surface area, pore volume and the pore size of the synthesized adsorbent.

2.4. Performance evaluation of the adsorbent for post-combustion CO2 capture

Adsorption set-up depleted in Figure 1 was used to evaluate the CO2 adsorption performance of the synthesized sod-ZMOF-chitosan. The set-up consisted of a packed-bed column connected to a CO2 detector in order to read the CO2 concentration before, during and after adsorption. About 0.05 g of the adsorbent was packed in the column. The sample in the column was then heated from room temperature to 110 °C under continuous flow of nitrogen through the sample and held for another 30 minutes at 110 °C to remove impurities such as moisture from the adsorbent. Then the temperature was reduced to 25 °C. A gas mixture, containing 15% CO2 and 85% N2, was passed through the sample at a flow rate of 50 ml/min and a pressure of 1 bar for 1 h. The initial CO2 concentration in the feed stream was determined using a gas analyser by by-passing the adsorption column. Amount of CO2 adsorbed during the experiment was obtained according to Becnel et al. [15] using Equation (1):

$$q = \frac{y_f Q_f (1-P_f) T_s}{R T_s} - \frac{y_f P_f P_b}{R T_b} \frac{m_{adsorbent}}{m_{adsorbent}}$$

Where q is the amount of CO2 adsorbed in mol/g adsorbent (to express the amount in mg CO2/g adsorbent, q was multiplied by the molar mass of CO2), $y_f$ is the mole fraction of CO2 in the feed, $Q_f$ is the volumetric flow rate of the feed stream. $P_f$ and $T_s$ are the standard pressure and temperature, respectively. R is the universal gas constant; $\varepsilon_T$ is the total porosity of the bed; $m_{adsorbent}$ is the mass of the adsorbent and $t_a$ is the adsorption time. The aforementioned procedure was repeated at 40 °C, and 70 °C with constant feed flow rate and then repeated for varying feed flow rate keeping temperature and pressure constant at 25 °C and at 1 bar, respectively. The gas mixture employed in the study was used to mimic the composition of flue gas expected from a typical coal-fired power plant.
3. Results and Discussion

3.1. Physicochemical characterization

Figure 3 depicts the XRD patterns of sod-ZMOF before and after chitosan impregnation. XRD pattern of sod-ZMOF was compared with those from Calleja et al [16] which confirmed that the synthesized material is crystalline and similar to that reported in literature. XRD pattern were obtained for chitosan impregnated sod-ZMOF in order to determine if sod-ZMOF maintained its crystallinity after chitosan impregnation. The XRD pattern of chitosan impregnated sod-ZMOF shows a similar shape to that of sod-ZMOF. This indicates that the structure of sod-ZMOF was still conserved after chitosan impregnation.
The FTIR spectra of sod-ZMOF and sod-ZMOF-chitosan are depicted in figure 4. The organic linker in sod-ZMOF is 4,5-Imidazoledicarboxylic acid and as such it is expected that sod-ZMOF and this organic linker have similar functional groups. The functional groups present in 4,5-Imidazoledicarboxylic acid are amine (N-H), carboxylic acid (O-H), aromatics (C-C (in ring)), aromatic amine (CN) and (C=O). The FTIR analysis of sod-ZMOF in Figure 3 shows the presence of COOH at a wavelength of 3178 cm\(^{-1}\), C-C (in ring) at a wavelength of 1476 cm\(^{-1}\), C-N at a wavelength of 1105 cm\(^{-1}\), N-H at a wavelength of 779 cm\(^{-1}\) and C=O at a wavelength of 1700 cm\(^{-1}\), which therefore confirms the successful synthesis of sod-ZMOF. Refer to table 1 for interpretation. Figure 3 also shows FTIR spectrum for sod-ZMOF-chitosan. The FTIR spectrum of sod-ZMOF-chitosan showed functional groups similar to those found in sod-ZMOF. However, there is a drastic decrease in the intensity of the O-H (carboxylic acid) band in the spectrum for sod-ZMOF-chitosan as compared to the ordinary sod-ZMOF. When Chen et al. [10] grafted sod-ZMOF with ethylenediamine (EDA), the FTIR also showed a decrease in O-H band after grafting. Chen et al. [10] speculated that the decrease in O-H band could be as a result of carboxylic acids being transformed to amide groups. In this work, the decrease in the O-H band could also be due to the impregnation of chitosan which then confirms the presence of chitosan (amine group) in sod-ZMOF chitosan.
Figure 3: FTIR spectra of sod-ZMOF before and after chitosan impregnation

Table 1: Interpretation of characteristics of IR absorption

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3.2. Surface area and pore volume

The Nitrogen physi-sorption at 77 K was conducted on sod-ZMOF before and after chitosan in order to determine the pore volume and BET surface area. Table 2 shows a summary of the results obtained in this study. From work done by Chen et al. [8], sod-ZMOF has a pore volume of 0.16 cm³/g and a BET surface area of 375 cm²/g. In this study, sod-ZMOF had a pore volume and BET surface which were much less than that from the work done by Chen et al. [8]. The low pore volume and the BET surface area could be attributed to the presence of material such as Structure Direction Agent (SDA) occluded in the structure that was not completely removed. In order to remove the occluded material from the sod-ZMOF, drying temperature was increased from 100°C to 150°C. However, this resulted in the structure of sod-ZMOF being affected as the FTIR spectra in Figure 4 illustrates the FTIR spectra of the sod-ZMOF where drying occurred at 100°C and 150°C are different. The carboxylic acid at a wavelength of about 3116 cm⁻¹ completely disappeared for the sod-ZMOF that was dried at 150°C as compared to the one dried at 100°C. This shows that the structure of sod-ZMOF was affected. This is expected as metal organic frameworks are unstable at high temperatures [17]. As this study is preliminary, effort will be made to remove the material from the structure in the subsequent optimization study of the material.

In addition, impregnation of chitosan on sod-ZMOF resulted in a decrease in surface area and pore volume. The decrease in surface area and pore volume is expected as chitosan impregnated occupies the surface area and pore volume in sod-ZMOF. The decrease in surface area is a significant indication of the successful impregnation of chitosan. Chen et al. [8] also observed a decrease in surface area and pore volume when they grafted amine onto
sod-ZMOF.

3.3. CO₂ adsorption performance

CO₂ adsorption performance of sod-ZMOF-chitosan was evaluated using the adsorption set-up depicted in Figure 1. The performance evaluation of sod-ZMOF-chitosan was determined using a gas mixture containing CO₂ (15%) and N₂ (85%). During the indication of the CO₂ by the gas analyser, the CO₂ reading starts to decrease with time indicating that some of the CO₂ was adsorbed onto the adsorbent from the inlet stream. After a certain time, the gas analyser displayed an increase in the CO₂ concentration until it reached the initial concentration in the feed stream, indicating the completeness of the adsorption process. Figure 2 depicts the CO₂ concentration profile of the adsorption process as obtained from the CO₂ gas analyser.

![Figure 4: CO₂ concentration profile from the adsorption process](image)

Figure 5 depicts the adsorption performance of sod-ZMOF-chitosan as a function of temperature. Adsorption capacity is increased with decreasing in temperature. At the lowest temperature of 25°C, adsorption capacity was 978 mg CO₂/ g adsorbent and reduced to 546 mg CO₂/ g adsorbent at 70°C. This is expected as adsorption is an exothermic process [15]. When gas molecules come into contact with the adsorbent, the gas molecules are taken by the adsorbent and heat is generated (that is heat of adsorption) [18]. Increasing temperature increases the kinetic energy of gas molecules so at high temperatures thus CO₂ molecules have high kinetic energy and as such they spend less time on the adsorbent surface which results in low adsorption capacity at high temperature.
Figure 5: CO₂ adsorption performance of sod-ZMOF-chitosan as a function of temperature

Figure 6 depicts the results of the investigation of the CO₂ adsorption performance of the adsorbent at different feed flow rates. The CO₂ adsorption performance of sod-ZMOF-chitosan was evaluated at feed flow rates of 25, 50 and 70 ml/min keeping constant temperature and pressure at 25°C and at 1 bar, respectively. Amount of CO₂ decreased with increase in the feed flow rate. At the lowest flow rate of 25 ml/min, the amount of CO₂ adsorbed by sod-ZMOF-chitosan was 978 mg CO₂/g adsorbent, and at a high flow rate of 70 ml/min, the mount of CO₂ adsorbed was 170 mg CO₂/g adsorbent. This behaviour could be attributed to the reduction in the contact time between the adsorbate and the adsorbent at higher feed flowrates. More contact time means the gas spends more time at the surface of the adsorbent thus more gas molecules will be adsorbed.

Figure 6: CO₂ adsorption performance of sod-ZMOF-chitosan as a function of feed flowrate

Since some researchers commonly use TGA to investigate CO₂ adsorption performance of their adsorbents during post-combustion CO₂ capture, performance evaluation of our adsorbent was carried out using TGA as well at
different temperatures and feed flowrates. The CO₂ adsorption performance of our adsorbent with the use of TGA was similar to that observed when the packed-bed adsorption column was used. Figure 7 and Figure 8 depict the CO₂ adsorption performance of our adsorbent using TGA. However, the amount of CO₂ adsorbed obtained when a TGA was used was much less than that obtained using the packed-bed adsorption column, even at 100% CO₂ which was used for the TGA. In a packed-bed adsorption column, mass transfer between the adsorbent and adsorbate (CO₂) is greatly enhanced. This is because with a packed-bed adsorption column, the gas flows through the packed adsorbent particles while with the TGA; the gas just flows over the sample pan that contains the adsorbent with little contact with the adsorbent particles.

Figure 7: CO₂ adsorption performance of sod-ZMOF-chitosan as a function of temperature using TGA

Figure 8: CO₂ adsorption performance of sod-ZMOF-chitosan as a function of feed flowrate using TGA.
4. Conclusion

In this work sod-ZMOF-chitosan was successfully synthesized and evaluated for CO₂ capture. XRD analysis showed that sod-ZMOF maintained its crystallinity after chitosan impregnation. FTIR and BET analysis showed successful impregnation of chitosan onto sod-ZMOF. The highest amount of CO₂ adsorbed was 2132 mg CO₂/g adsorbent at 25°C, 50 ml/min and 1 bar. In addition, amount of CO₂ adsorbed decreased as temperature and feed flowrates were increased.

5. Acknowledgements

The authors acknowledge the financial assistance from the National Research Foundation (NRF) of South Africa, the South African Centre for Carbon Capture and Storage (SACCCS) and the University of the Witwatersrand (WITS). In addition, the authors thank ABB for the provision of the gas detector utilized in this research.

References


Modelling and Experimental Study of the CO₂ Adsorption Behaviour of Polyaspartamide as an Adsorbent during Post-Combustion CO₂ Capture

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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 CO₂ 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 CO₂ 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 CO₂ adsorption onto polyaspartamide. The kinetics of adsorption of polyaspartamide was studied using Lagergen’s
pseudo 1\textsuperscript{st} order, Lagergen’s pseudo 2\textsuperscript{nd} 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\textsubscript{2} onto polyaspartamide while the kinetic study revealed that the mechanism of adsorption of CO\textsubscript{2} onto polyaspartamide was more of physical than chemical (physiochemical).

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**Keywords:** Adsorbents; Adsorption; Breakthrough curves; CO\textsubscript{2} capture; Polyaspartamide;

1. **Introduction**

The interest in CO\textsubscript{2} capture is rising continuously around the globe. Carbon capture and storage (CCS) is a promising technology for mitigating climate change and meeting CO\textsubscript{2} emission reduction targets [1]. Anthropogenic CO\textsubscript{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\textsubscript{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\textsubscript{2} capture via the adsorption technology ensures that the adsorbent is in direct contact with the CO\textsubscript{2} gas in an adsorption column. Mathematical models describing the behavior of the adsorbent during the post-combustion CO\textsubscript{2} capture is very essential in designing, optimizing and scaling-up of the CO\textsubscript{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\textsubscript{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. CO₂ capture using solid adsorbents involves a selective separation of CO₂ 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 CO₂ 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 CO₂ capture [9]. This simply means that adsorbents play a key role in any adsorption technology [15]. For instance, adsorbents determine the overall CO₂ capture performance in the vacuum swing adsorption (VSA) technology [16]. The key elements for a good adsorbent in CO₂ capture technology are; high selectivity of CO₂, 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 CO₂ 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 CO₂ 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 CO₂ capture using a balanced flue gas stream of 15% CO₂ and 85% N₂. This study focused on investigating the adsorption behavior of polyaspartamide as an adsorbent during post combustion CO₂ capture using mathematical modeling and experimental validation approach. Other properties to test for the performance of polyaspartamide during CO₂ capture such as adsorption kinetics was also studied using kinetic models.

<table>
<thead>
<tr>
<th>Nomenclature</th>
</tr>
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<tbody>
<tr>
<td>% E</td>
</tr>
<tr>
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</tr>
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<td>Kₙ</td>
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</tr>
<tr>
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</tr>
<tr>
<td>qₑ</td>
</tr>
<tr>
<td>Qₑₓᵖ</td>
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<tr>
<td>Qₘ₀</td>
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<tr>
<td>qₜ</td>
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<tr>
<td>t</td>
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<tr>
<td>VSA</td>
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</tbody>
</table>

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 CO₂ and N₂ (15% CO₂, 85 % N₂) 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

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

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 CO₂ 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 N₂ flow. The flue gas mixture (15% CO₂, 85 % N₂) 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 CO₂ 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 CO₂ uptake onto the polyaspartamide material was monitored as a function of time from the CO₂ 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 CO₂ 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.
<table>
<thead>
<tr>
<th>Models Studied</th>
<th>Assumptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bohart-Adams model</td>
<td>1. Rectangle or step isotherm is assumed for the model and adsorption bed is homogenous</td>
</tr>
<tr>
<td></td>
<td>2. Gradients occur only in the axial direction and they are negligible</td>
</tr>
<tr>
<td></td>
<td>3. At time t = 0, the bed is free of adsorbate (CO₂)</td>
</tr>
<tr>
<td></td>
<td>4. The model assumes that equilibrium is not instantaneous</td>
</tr>
<tr>
<td></td>
<td>5. Irreversible adsorption isotherm</td>
</tr>
<tr>
<td>Thomas Model</td>
<td>1. The axial and radial dispersion in the column is negligible</td>
</tr>
<tr>
<td></td>
<td>2. Constant separation factor</td>
</tr>
<tr>
<td></td>
<td>3. Adsorption is described by a pseudo-second order reaction rate principle and reduces to a Langmuir isotherm at equilibrium.</td>
</tr>
<tr>
<td></td>
<td>4. The column void fraction is constant</td>
</tr>
<tr>
<td></td>
<td>5. Constant temperature and pressure process conditions</td>
</tr>
<tr>
<td></td>
<td>6. Negligible external resistance during mass transfer process.</td>
</tr>
<tr>
<td>Lagergen's pseudo 1st order model</td>
<td>1. The rate of adsorption increases as the number of vacant site on the adsorbent increases</td>
</tr>
<tr>
<td></td>
<td>2. Local equilibrium is achieved instantaneously and the primary resistance is mass transfer resistance.</td>
</tr>
<tr>
<td>Lagergen's pseudo 2nd order model</td>
<td>1. The rate of adsorption is proportional to the square of the number of vacant sites</td>
</tr>
<tr>
<td>Avrami kinetic model</td>
<td>1. There are random nucleation sites across the reaction surface</td>
</tr>
</tbody>
</table>
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 CO2 (C/Co) 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.
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
The 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 CO₂ 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):

\[
\% E = \sqrt{\frac{\sum_{i=1}^{N} (\frac{Q_{exp} - Q_{mod}}{Q_{exp}})^2}{N-1}} \times 100
\]

Where \( % E \) is the error function from the study in percentages, \( Q_{exp} \) is the average amount of CO₂ adsorbed experimentally at a given time, \( Q_{mod} \) is the amount of CO₂ adsorbed as predicted by the mathematical model and \( N \) is the total number of experimental runs.

The CO₂ capture efficiency of the adsorbent was calculated on percentage basis by dividing the equilibrium concentration of CO₂ by the initial CO₂ concentration according to Equation 2.

\[
\% \text{ CO₂ capture efficiency} = \frac{C_e}{C_o} \times 100
\]

Where \( C_e \) is the gas concentration at equilibrium and \( C_o \) is the initial concentration of the gas. The percentage CO₂ capture efficiency was obtained at all temperatures considered in this study using Equation 2 and presented in Table 3.
Table 3. CO₂ capture efficiency of polyaspartamide at different adsorption temperatures and constant pressure.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pressure (bar)</th>
<th>CO₂ capture efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>2</td>
<td>92.67</td>
</tr>
<tr>
<td>318</td>
<td>2</td>
<td>90.00</td>
</tr>
<tr>
<td>333</td>
<td>2</td>
<td>86.67</td>
</tr>
</tbody>
</table>

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 CO₂ capture system. The Lagergen’s pseudo 1\textsuperscript{st} order, pseudo 2\textsuperscript{nd} order and Avrami kinetic models were used to investigate the kinetics of adsorption CO₂ onto polyaspartamide as presented in Figure 5. The Lagergen’s pseudo 1\textsuperscript{st} and 2\textsuperscript{nd} order kinetic models had some limitations with respect to the adsorption of CO₂ onto polyaspartamide. After few seconds, the Lagergen’s pseudo 1\textsuperscript{st} order model under-estimated the uptake of CO₂ till about 120 seconds and afterwards, CO₂ 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 1\textsuperscript{st} 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 CO₂ 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 CO₂ onto polyaspartamide could be described as a physiochemical process. The kinetic constant of the Avrami model is independent
of the initial concentration of CO₂. 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 CO₂ 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 CO₂ on polyaspartamide

<table>
<thead>
<tr>
<th>Kinetic models</th>
<th>Parameters</th>
<th>303 K</th>
<th>318 K</th>
<th>333 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first order model</td>
<td>Kf (s⁻¹)</td>
<td>3.2 x 10⁻²</td>
<td>3.53 x 10⁻²</td>
<td>3.92 x10⁻²</td>
</tr>
<tr>
<td></td>
<td>Error (%)</td>
<td>1.33</td>
<td>5.27</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>qₑ (mol g⁻¹)</td>
<td>4.97</td>
<td>4.72</td>
<td>4.37</td>
</tr>
<tr>
<td>Pseudo-second order model</td>
<td>Ks (gmol⁻¹s⁻¹)</td>
<td>2.24 x 10⁻²</td>
<td>3.14 x 10⁻²</td>
<td>4.42 x10⁻²</td>
</tr>
<tr>
<td></td>
<td>Error (%)</td>
<td>8.81</td>
<td>3.88</td>
<td>2.33</td>
</tr>
<tr>
<td></td>
<td>qₑ (mol g⁻¹)</td>
<td>5.2</td>
<td>4.82</td>
<td>4.4</td>
</tr>
<tr>
<td>Avrami model</td>
<td>KA (s⁻¹)</td>
<td>3.99 x 10⁻²</td>
<td>4.17 x 10⁻²</td>
<td>4.31 x10⁻²</td>
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<tr>
<td></td>
<td>Error (%)</td>
<td>2.38</td>
<td>2.22</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td>qₑ (mol g⁻¹)</td>
<td>5.74</td>
<td>4.94</td>
<td>4.45</td>
</tr>
<tr>
<td></td>
<td>nA</td>
<td>1.76</td>
<td>1.46</td>
<td>1.38</td>
</tr>
</tbody>
</table>
The graph shows the experimental data and the predictions of three different kinetic models: Pseudo 1st order model, Pseudo 2nd order model, and Avrami model. The x-axis represents time (sec) and the y-axis represents q (mol/kg). The data points (black dots) are compared with the lines representing the models. The legend indicates the different models and their symbols.

- Experiment: Black dots
- Pseudo 1st order model: Blue line
- Pseudo 2nd order model: Green dashed line
- Avrami model: Red dashed line
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.
From the results of the Bohart-Adams model (non-kinetic model), it can be logically concluded that mass transfer dominated the adsorption of CO₂ 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 CO₂ onto polyaspartamide at all temperatures studied as shown in Figure 5. This simply implies that the adsorption of CO₂ onto polyaspartamide is more of a physical than chemical adsorption process (Physiochemical). Increasing the feed (i.e. CO₂) 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 CO₂ adsorbed by polyaspartamide. This simply means that, longer breakthrough times are required for a higher amount of CO₂ to be adsorbed by polyaspartamide which subsequently results to a higher adsorption capacity.

Acknowledgements

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