

CERTIFICATION OF APPROVAL


Carbon Dioxide Adsorptive Removal using Modified Molecular Sieve

By

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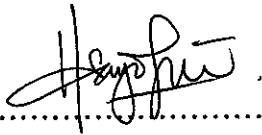
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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgments, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



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ABSTRACT

Global warming is one of the main serious problems due to elevated index of carbon dioxide in the atmosphere. Recently, CO₂ captures have been receiving significant attention and are being recognized. Nowadays, amine based chemical absorption is one of the famous technologies used in separation of CO₂. However, the liquid amine based processes is not really preferable because of several weakness such as high regeneration energy, large equipment size, solvent leakage and corrosion problem. Adsorption technology which is less energy intensive is known as proficient for CO₂ separation method since it is predicted to have low requirement of energy for porous adsorbent regeneration while offer high productivity and selectivity. In this study, mesoporous molecular sieve was modified using monoethanolamine for CO₂ adsorption process. The materials were characterized by X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) experiment. The carbon dioxide sorption on modified molecular sieve was investigated using bench scale gas adsorption equipment at different pressure and temperature. The modified mesoporous molecular sieve results in better CO₂ adsorption capacity compared to unmodified molecular sieve relating to the existence of amine density in this material.

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CHAPTER 1

INTRODUCTION

1.1. BACKGROUND STUDY

The low quality of natural gas is due to some contaminants like nitrogen and carbon dioxide (CO₂). Due to high emissions of CO₂ from this fossil fuel combustion, the concentration of CO₂ in the atmosphere will increase and become a serious issue with respect to its effect on global warming. There are chemical and physical methods for removal of CO₂. Nowadays, chemical absorption is one of the famous technologies used in CO₂ removal at low pressure. Alkanolamines are widely used because of the high reactivity, ease of reuse and low absorption of hydrocarbons. The gas is subsequently released at high temperatures with a complicated chemistry when these amines react with CO₂ at low temperature. However alkanolamines has several weakness such as such alkanolamines/water solution are very corrosive and the energy consumption is too high for economic post combustion gas separation, generally because of the CO₂ recovery process due to high heat capacity of mixture. Besides that, amines and water may enter the gas stream, which limits the process applicability from the environmental and separation efficiency perspectives (Guoying.Z, 2010). Therefore, adsorption becomes the most attractive methods to CO₂ removal as it offer less energy intensive compared to absorption method that required high energy.

Porous adsorbents, with a relatively low heat capacity and high surface area are very promising candidates for low cost CO₂ capture and separation. Various adsorbents such as zeolite, activated carbon, silica gels and carbon molecular sieve were used but these conventional adsorbents were not effective to adsorb CO₂ because its adsorption capacity declined rapidly at high temperature even though it can adsorb high CO₂ at ambient temperature. Therefore, high surface area adsorbent such as mesoporous molecular sieve is required to develop high CO₂ adsorption capacity and a high CO₂ selectivity (N.H Alias a, 2010).

1.2. PROBLEM STATEMENT

1.2.1 Problem Identification

CO₂ is the major greenhouse gas causing global warming. Currently, adsorption has generated some attention in the CO₂ removal process due to less energy intensive. There were so many porous solid adsorbents that have been investigated as a medium for CO₂ removal. However these adsorbents results in low adsorption capacity with the increasing temperature. Hence the mesoporous molecular sieve is the best preference to capture CO₂ by adsorption because of its ability to operate at high temperature.

1.2.2 Significant of the Project

As adsorption is the most preferable method in removal of CO₂, developing solid sorbents with high selectivity and high adsorption capacities for carbon dioxide is very vital because such materials are more environmental friendly and easier to handle in solid forms as well as able to regenerate under mild condition thus more energy efficient.

Besides that, this project mainly developing an adsorbent through modification of mesoporous molecular sieve in order to produce an adsorbent which can operate at relatively high temperature and it is desired for more efficient CO₂ removal by an adsorption method.

1.3. SCOPE OF STUDY

This study will be focusing on develop adsorbent for CO₂ removal using modified molecular sieve to have higher CO₂ adsorption capacity. This study is in the form of laboratory experiments using bench scale equipment that required several types of mesoporous molecular sieve to be investigated at different operating conditions. Before that the molecular sieve will be modified using monoethanolamines (MEA) and the characterization of each modified molecular sieve will be analyzed using XRD and FTIR.

1.4. OBJECTIVES

The following list shows the several objectives to be achieved from this project:

1. To modify adsorbent (molecular sieve) using monoethanolamine (MEA).
2. To analyze the characterization of physical and chemical properties of modified molecular sieve.
3. To investigate the adsorption capacity of modified molecular sieves at different conditions of temperature and pressure.
4. To determine adsorption isotherm of the modified molecular sieve.

1.5. RELEVANCY OF THE PROJECT

Since the CO₂ can cause some other detrimental effects to living creatures and environment, treatment is necessary. As adsorption is the most effective method for CO₂ removal, the best adsorbents should be developed to increase the capacity of adsorption process. In addition, if this project succeeds in creating an advance technology in capturing CO₂, it will able to preserve the environment and reduce the emission of hazardous gas to the atmosphere and will prevent the greenhouse effect.

1.6. FEASIBILITY OF THE PROJECT

The following are the aims to be achieved for the final year project :

1. Review literature related to the topic
2. Preparing all the chemicals
3. Modification of molecular sieve using amines
4. Analyze the characteristic of modified molecular sieve
5. Lab experiment (CO₂ adsorption process) using modified molecular sieve
6. Analyze the result of experiment

CHAPTER 2

LITERATURE REVIEW

The phenomenon of global warming is worrying and become a serious problem due to excessive and elevated amount of CO₂ in the atmosphere. There are many techniques that can capture CO₂ such as amine absorption, membrane separation, cryogenic separation, and adsorption process. The most technology use for CO₂ removal is amine absorption but it is not very convenient because amine plants is very complex and costly (White CM, 2003; Song C, 2006). Thus, adsorption in porous materials is very well known because of its efficiency and economically competitive.

2.1. ADSORPTION PROCESS

Adsorption is a phenomenon of a surface on which a molecule contained in a fluid (gas or liquid) is fixed on the surface of a solid (José A. Delgado, 2007). Most of the physical, chemical and biological processes take place at the boundary between two phases, while others are initiated at that interface. The term 'adsorption' deals with the process in which molecules accumulate in the interfacial layer, but desorption denotes the converse process.

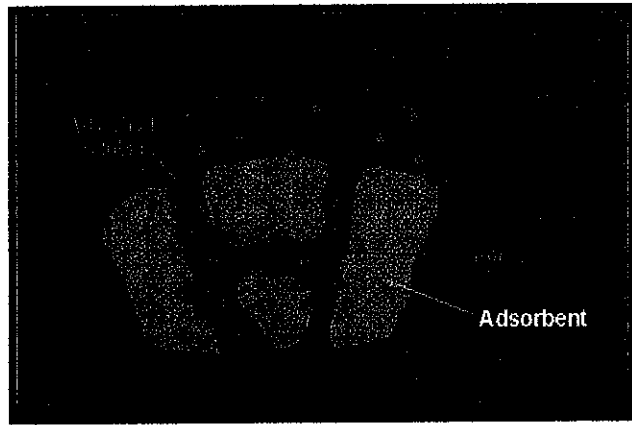


Figure 2.1: Illustration of bulk fluid phase

Adsorption hysteresis is said to occur when the adsorption and desorption curves deviate from one another. In such a case the isotherm possesses a hysteresis loop, the shape of which varies from one adsorption system to another. Hysteresis loops are mostly with mesoporous solids, where the so-called capillary condensation occurs. The material in the adsorbed state is defined as the 'adsorbate', but that in the bulk gas or vapor phase prior to being adsorbed is called the 'adsorptive'. The penetration by the adsorbate molecules into the bulk solid phase is determined as 'adsorption' (Sing, 2004; Sing, 1998; Dabrowski, 2001).

Based on the article written by UOP, with molecular sieve powders, no hysteresis occurs during desorption. Adsorption and desorption are completely reversible with their respective isothermal curves coinciding completely. However, with molecular sieve pellets or beads, further adsorption may occur at pressure near the saturation vapor pressure. This can occur as a result of condensation in the pellet or bead voids external to the zeolite crystals. In addition, hysteresis may take place during desorption of the adsorbate in the macro-pore region of the binder.

There are two method of adsorption which is physisorption and chemisorptions (Sing, 1998; Dabrowski, 2001). The characterization of these two methods is shown as per table below:

Table 2.1: Physisorption and Chemisorption

<u>Physical adsorption</u>	<u>Chemisorption</u>
<ul style="list-style-type: none"> ▪ Van der Waals adsorption ▪ Low heat of adsorption ▪ Non specific ▪ Monolayer or multilayer ▪ No dissociation of adsorbed species ▪ Only significant at relatively low temperatures ▪ Rapid, non-activated, reversible ▪ No electron transfer 	<ul style="list-style-type: none"> ▪ Activated adsorption ▪ High heat of adsorption ▪ Highly specific ▪ Monolayer only ▪ May involve dissociation ▪ Possible over a wide range of temperature ▪ Activated, may be slow and irreversible ▪ Electron transfer leading to bond formation between adsorbate and surface

Pressure Swing Adsorption (PSA) is a technology used to separate some gas species from a mixture of gases under pressure according to the species molecular characteristics and affinity for an adsorbent material. Pressure Swing Adsorption (PSA) technology is widely used because it offer less energy requirement and low capital investments cost. It operates at near-ambient temperatures and so differs from cryogenic distillation techniques of gas separation. Special adsorptive materials (e.g., zeolites) are used as a molecular sieve, preferentially adsorbing the target gas species at high pressure. The process then swings to low pressure to desorb the adsorbent material (12Fe).

Developing an adsorbent with high CO₂ adsorption capacity which can also be operated at high temperature is desired for more efficient CO₂ capture by adsorption method. Porous adsorbent is an excellent choice for low cost CO₂ capture as its offer a relatively low heat capacity and high surface area. Therefore, the study on molecular sieve was increased with respects to its efficiency in the adsorption process (José A. Delgado, 2007).

2.2. MOLECULAR SIEVES

Porous materials have becomes very attractive to the chemist and material scientist due to their commercial interest in the application in chemical separations and heterogeneous catalysis as well as scientific interest in the challenge posed by their synthesis, processing, and characterization. The discovery of the first ordered mesoporous molecular sieve has great interest throughout the scientific community. These materials possessing pore size in the 2-50nm range have a broad potential of applications such as shape-selective catalysis and sorption of large organic molecules, chromatographic separations, and uses as hosts to confine guest molecules and atomic arrays. On top of that, the unique properties of these materials such as highly ordered pore structure, high surface area, tunable pore size or the ability to tailor framework, high hydrothermal and mechanical stabilities, large pore volumes and high density of surface silanol have make these materials advanced compare to other materials (Barton *et al*,1999).

The mesoporous molecular sieves are synthetic zeolites or metal alumino silicates, with a porous tridimensional crystallized network. Molecular sieves have high adsorption capacity for relatively low concentration of the adsorbate which makes it differ from other adsorbents in the shape of their isotherms. The increasing of the adsorption capacity

with respect to the increasing of temperature is another important characteristic of molecular sieve.

Other beneficial performance characteristics include (UOP):

- Dehydration to water content less than 0.1ppm
- High capacity for water above 200F (93C)
- Purification and dehydration in one operation
- Dehydration without adsorbing valuable product or altering the composition
- High product recovery
- Numerous purification and dehydration cycles are possible due to the reversible adsorption process
- High cyclic capacity with sufficient thermal or pressure swing purging

Based on UOP article also, the rate at which molecules are adsorbed into formed molecular sieve depends on the following four variables:

- The rate at which molecules being adsorbed can diffuse to activated crystals within the pellet or bead
- The relative size of molecules and molecular sieve pores
- The strength of adsorptive forces between molecular sieves and adsorbate
- Adsorption temperature

Specific and uniform pore size is the key to adsorbent efficiency and selectivity. Based on size and charge distribution in a molecule, molecular sieves can adsorb individual molecules readily and slowly. Molecular sieves have regular pore size, they are called 3, 4, 5 or 10Å although the real pore opening is somewhat lower to these values (CECA Arkema Group, 2011).

Table 2.2: Types and applications of molecular sieves

Types of molecular sieve	Application
3Å	Drying of Olefin, Jet Fuel, Kerosene, Alkylation Feed, Hexane, Benzene, Ethylene, Propylene, Methanol, Ethanol and Isopropanol.
4Å	Drying of Hydrogen Rich Gas, Hydrocracker Gas and Natural Gas. H ₂ S and CO ₂ removal Drying of fluorocarbons for Refrigeration Systems
5Å	Drying, desulphuration, CO ₂ removal of natural gas. Drying and CO ₂ removal of air Nitrogen production plant.
13X	Air Plant Feed Drying and CO ₂ removal. Natural Gas Mercaptan Removal. LPG Sweetening ; H ₂ S and Mercaptan Removal LNG Plant Feed Pretreatment; H ₂ S, CO ₂ , Mercaptan Removal.

The significance of pores in the adsorption processes largely depends on their sizes. Because sizes of micropores are comparable to those adsorbate molecules, all atoms or molecules of the adsorbent can interact with the adsorbate species. That is the fundamental difference between adsorption in micropores and larger pores like mesopores and macropores. Consequently, the adsorption in micropores is essentially a pore-filling process in which their volume is the main controlling factor (Dabrowski, 2001). The basic parameters characterizing mesopores are:

- Specific surface area
- Pore volume
- Pore size or pore volume distribution.

Recently, the modified mesoporous molecular sieves show the increasing number of studies for different applications. For the CO₂ capture, in order to have high adsorption capacity and selectivity the surface of these materials should be modified. In previous studies, mesoporous material was modified using monoethanolamine (MEA) on the surface of the solid adsorbent to separate CO₂-N₂. Amine functional groups has ability to form ammonium carbanates and carbonate reversibly at moderate temperature, therefore it is very useful for CO₂ removal.. From the research work, amine-modified mesoporous molecular sieve able to improve CO₂ adsorption capacity (N.H Alias a, 2010).

2.3. ADSORPTION ISOTHERM

The fundamental concept in adsorption process is named as the adsorption isotherm. It is an equilibrium relation between the amounts of adsorbate adsorbed on the surface of adsorbent and the pressure or concentration in the bulk fluid phase at constant temperature. Apart from the results of the calorimetric measurements, the adsorption isotherm is the primary source of information on the adsorption process.

The concept of adsorption as related to an area of exposed surface was developed by Irving Langmuir in his work on the condensation of gases on surfaces. Based on his theory, he derived Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure (Suzuki.M, 1992).

$$\theta = \frac{KP}{1 + KP}$$

Where θ the number of sites of the surface which are covered with gaseous molecule, P represents pressure and K is the equilibrium constant for distribution of adsorbate between the surface and the gas phase .The basic limitation of Langmuir adsorption equation is that it is valid at low pressure only. At lower pressure, KP is so small, that factor (1+KP) in denominator can almost be ignored. So Langmuir equation reduces to

$$\theta = KP$$

At high pressure KP is so large, that factor (1+KP) in denominator is nearly equal to KP. So Langmuir equation reduces to

$$\theta = \frac{KP}{KP} = 1$$

Referring to the article written by UOP, since molecular sieves rely on strong physical forces rather than chemisorptions to retain adsorbates, their adsorption is characterized by a Langmuir-type isotherm (the amount of a given compound adsorbed increase rapidly to a saturation value as its pressure or concentration increase in the external bulk phase. Any further increase in pressure at constant temperature cause no further increase in the amount adsorbed. With molecular sieves, this equilibrium saturation value typically corresponds to a complete filling of the internal void volume with the adsorbate. When adsorbed molecules are desorbed via heat or by displacement with another material, the crystal's chemical state remains unchanged.

Porous materials are most frequently characterized in terms of pore sizes derived from gas sorption data, and IUPAC conventions have been proposed for classifying pore sizes and gas sorption isotherms that reflect the relationship between porosity and sorption. The IUPAC classification of adsorption isotherms is illustrated in figure below:

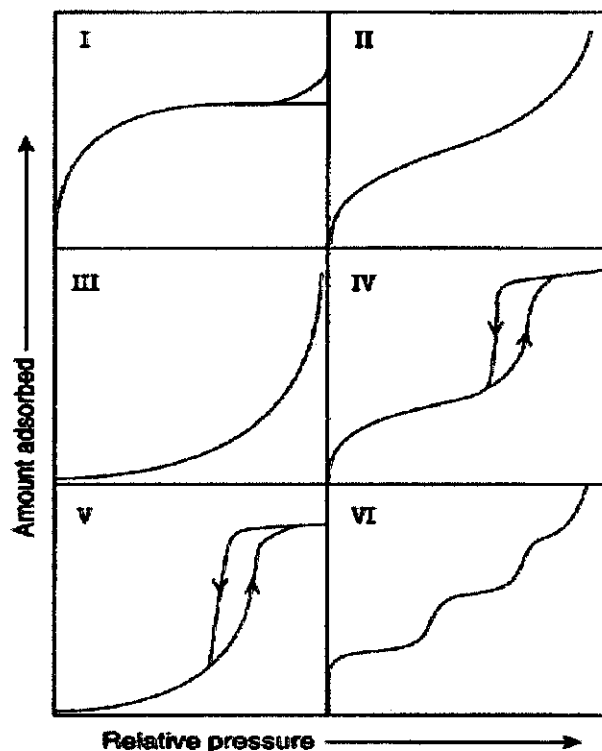


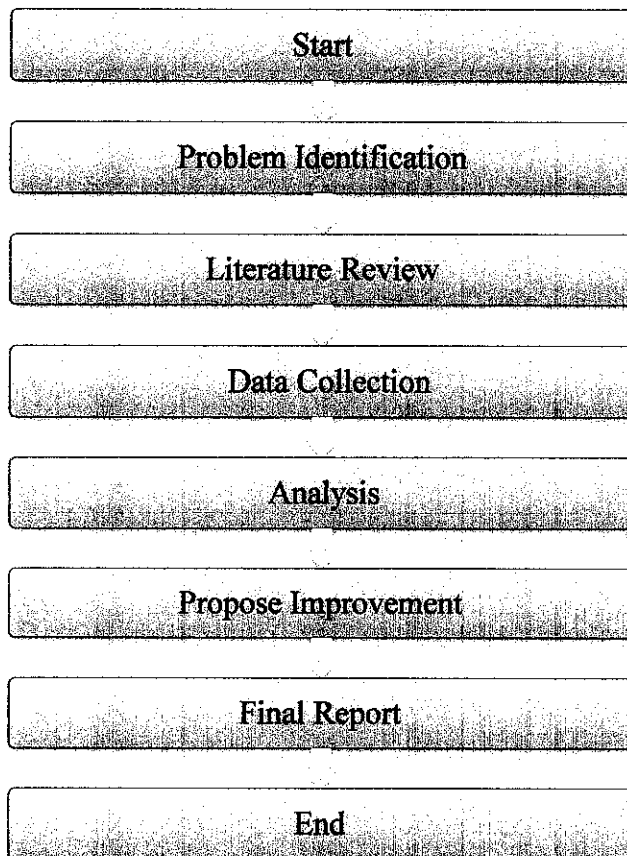
Figure 2.2: IUPAC classifications of adsorption isotherms

The six types of isotherm are characteristic of adsorbents that are microporous (type I), nonporous or macroporous (types II, III and VI) or mesoporous (types IV and V). The differences between types II and III isotherms and between types IV and V isotherms arise from the relative strengths of the fluid-solid interactions and types III and V are associated with weaker fluid-solid interactions. Types IV and V isotherms are usually exhibited which represent capillary condensation in the mesopores. While, the type VI isotherm represents adsorption on nonporous or macroporous solids where stepwise multilayer adsorption occurs (Kruk *et al.*,1999 ; Sing,2001; Barton *et al.*,1999; Ustinov *et al.*,2005).

CHAPTER 3

METHODOLOGY

3.1. PROJECT ACTIVITIES



3.2. METHODOLOGY

The project is a study to develop the adsorbent (modified mesoporous molecular sieve) in order to increase adsorption capacity in CO₂ adsorption process.

First and foremost, the project begin with identifying the problem statement. The problem identify for this project is high CO₂ released in the atmosphere from fossil fuel combustion that will contribute to the global warming which is harmful to the creature. Therefore, it shows that the efficiency of existing method to capture CO₂ is lower than what it should be.

After being clear with the problem, the project proceed with the literature review in order to get some background study and detailed understanding with the current CO₂ capture method. The literature review including the general explanation on adsorption method to capture CO₂, the basic information on adsorbent used in current method and also the clarification of adsorbent that will be used in this project. Besides that, the literature review discussed on the adsorption isotherm which is the fundamental concept in adsorption process.

With all the collective information from the literature review, a clear idea on the project was obtained. Then the project proceeds to the data collection. At this stage, an experiment was done. The experiment process includes the preparation process for mesoporous molecular sieve before it will go through the modification process. The characterization of modified mesoporous molecular sieve will be analyzed using XRD and FTIR. After that, the efficiency of modified mesoporous molecular sieve was tested and all the data regarding the experiment was collected.

Next, after all the data are properly taken, comes the most typical part of the project which is the analysis of the data. From experiment, the adsorption capacity for modified mesoporous molecular sieve was measured along with its adsorption isotherm.

3.3. MATERIALS AND CHEMICALS

Below is the list and details of the materials that were used for this study:

Materials	Carbon Dioxide (CO₂)	Monoethanolamine (MEA)	Molecular Sieve	Methanol
Source	Linde Gas	R&M Chemicals	Sigma Aldrich	Merck
Physical and Chemical Properties	Melting point/Melting range: -56.6°C Boiling point/Boiling range: -78°C Solubility in / Miscibility with Water at 20°C: 2000 g/l	Molecular weight :61.08g/mole pH:10 Boiling point : 170.8°C Melting point : 10.3°C Critical temperature :341°C Specific gravity :1.018 Vapor pressure : 0.1kpa (@20°C) Vapor density : 2.1	Type :13X Size :1.0nm BEADS 4-8 MESH	Boiling point :64.7°C Melting point :- 98°C Flash point :12°C LLE :6vol% ULE :31vol% Viscosity :0.55cP Vapor pressure :128hPa Molecular weight :32.04 g/mol Specific gravity: 0.792 g/cc

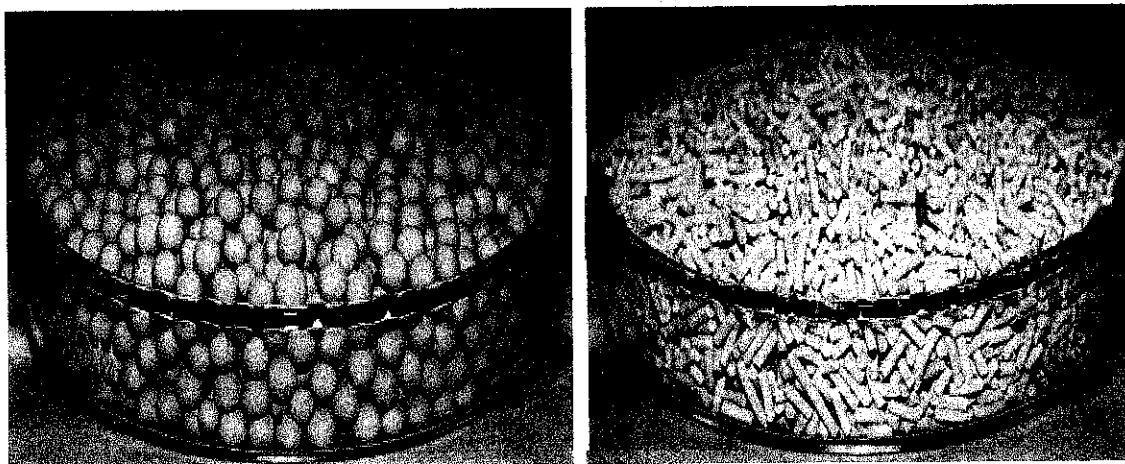


Figure 3.1: Molecular Sieve Type 13X

3.4. EXPERIMENTAL PROCEDURE

3.4.1 Preparation and Modification of Molecular Sieve

Before proceed to the modification process, the molecular sieve should be dry in oven at 60°C for 12hour. Then, mix 10g of molecular sieve in 50 mL of methanol. After that, add 20mL of the respective monoethanolamine (MEA) into the methanol and kept the suspension under reflux for 24 hour. Filter off the solid product and wash repeatedly with methanol and dried at 80°C in the oven. Lastly, analyze the characterization of modified molecular sieve using X-ray Diffraction (XRD) and Fourier Transform Infrared (FTIR).

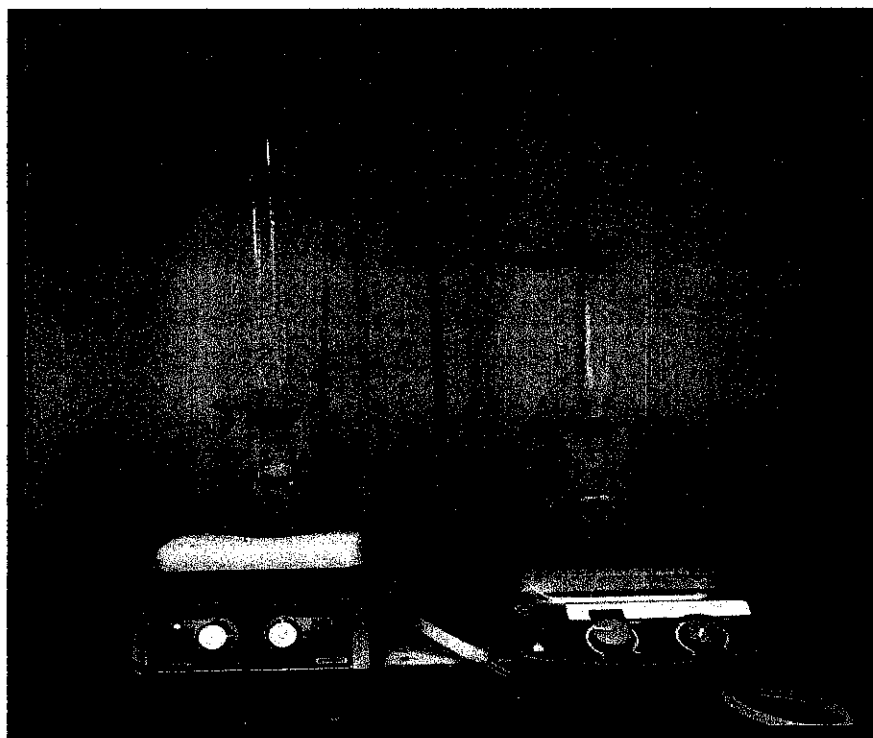


Figure 3.2: Amine modified molecular sieve under reflux

3.4.2 Gas Adsorption Reactor Procedure

1. Switch ON main power supply : RED indicator light turns ON.
2. Double click on the “High Pressure Mini” icon to initialize the software.
3. Open V1 for gas inlet from gas source.
4. Set inlet gas flow.
5. Set Present Value (PV) for temperature inside the reactor.
6. When it reach the desired temperature and pressure, click “RUN” to start the real time data acquisition link with reactor sensor.
7. Press “STOP” button to offline the software.

8. After finish the experiment OFF all valve and switch.
9. Close gas source.
10. Shutdown the PC and power OFF.

3.5. EQUIPMENTS

3.5.1 Main Equipments

The bench scale gas adsorption equipment will be used in the experiment of CO₂ adsorption process.

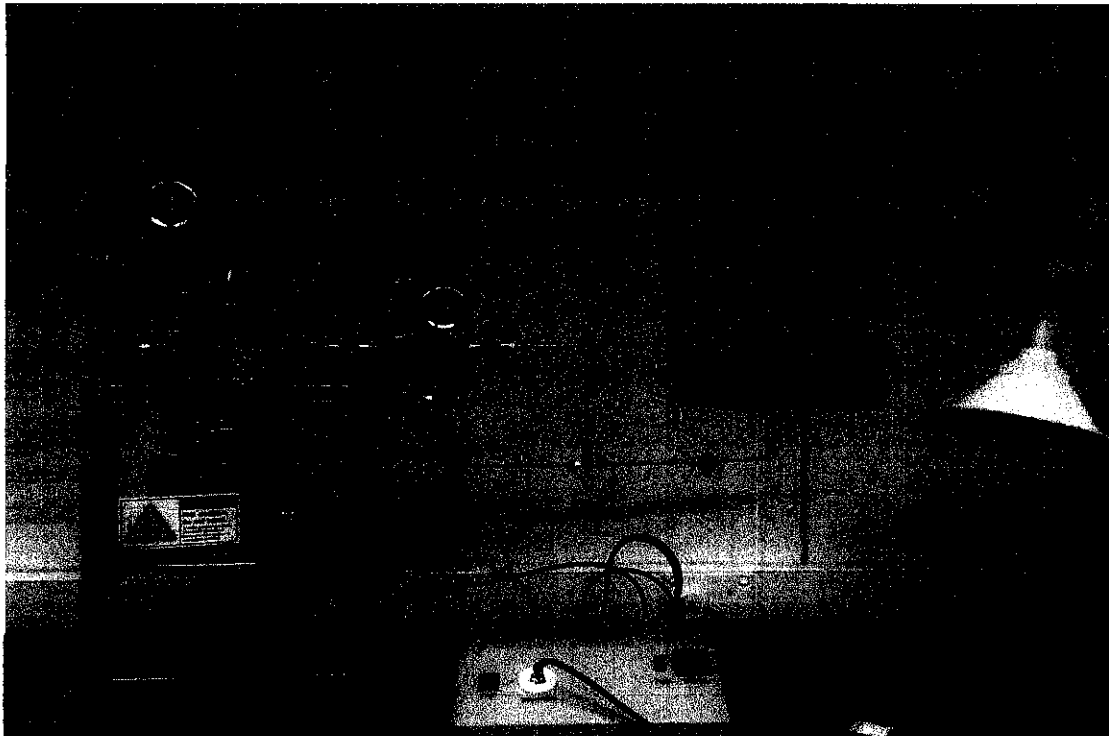


Figure 3.3: Bench scale gas adsorption equipment

3.5.2 Equipments for Adsorbent (Molecular sieve) Characterization

There are several types of equipments that can be used for characterization of adsorbent. For this project, the equipments involve including Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD).

i. Fourier Transform Infrared Spectroscopy (FTIR)

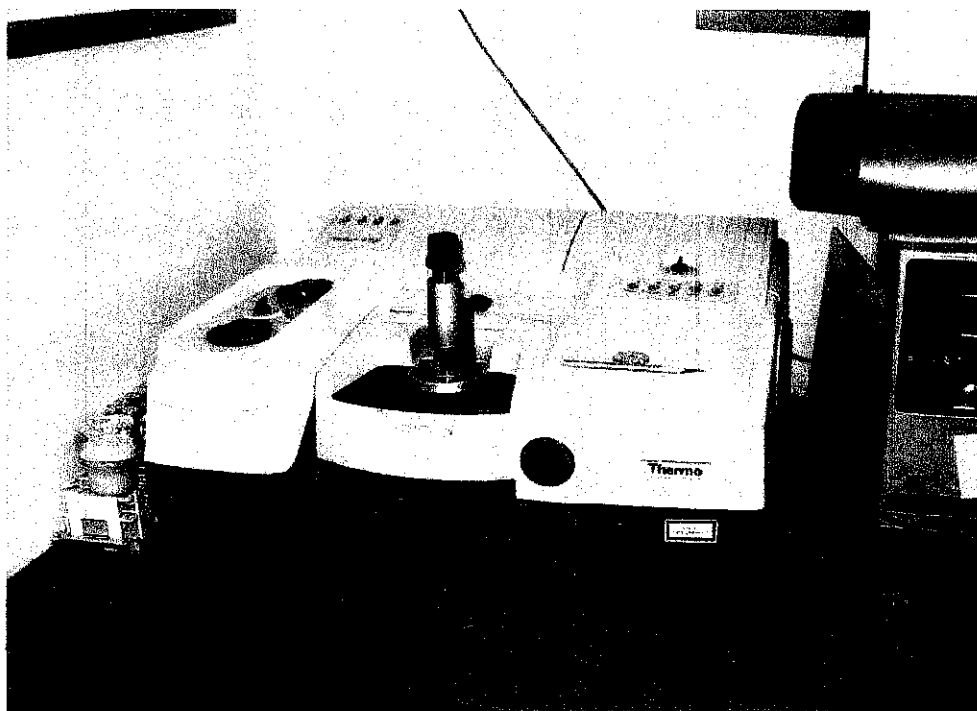


Figure 3.4: Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared (FTIR) is the preferred method of infrared spectroscopy. In infrared Spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. For most common material,

the spectrum of unknown can be identified by comparison to library of known compounds.

- Information listed below is the function of FTIR provided.
- It can identify unknown materials.
- It can determine the quality or consistency of a sample.
- It can determine the amount of components in a mixture.

ii. **X-ray Diffraction (XRD)**

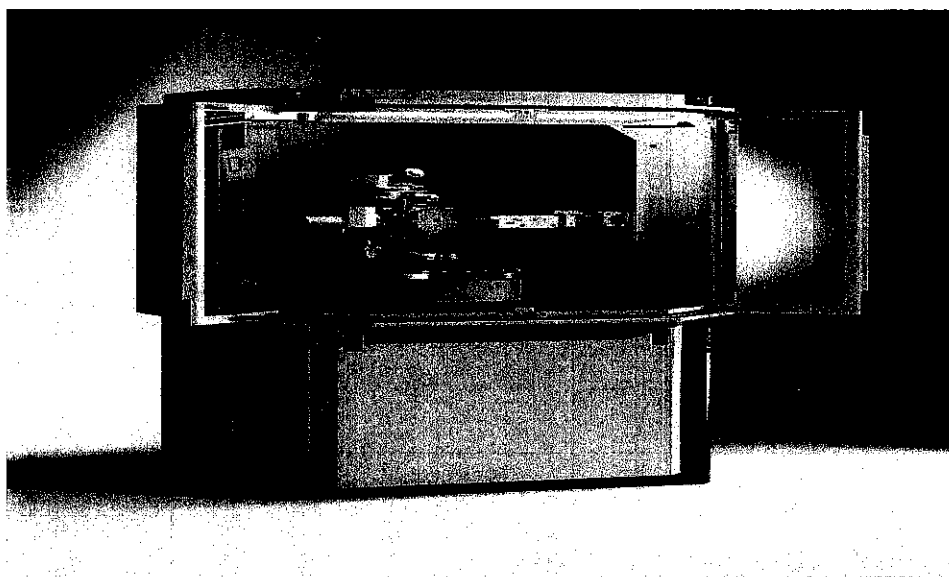


Figure 3.5: X-ray Diffraction (XRD)

X-ray diffraction, (XRD) is the primary method used to identify phases. When a monochromatic x-ray beam with wavelength λ is incident on the lattice planes in a crystal at an angle θ , diffraction occurs only when the distance traveled by the rays reflected from successive planes differs by a complete number of wavelengths. Plotting the angular positions and intensities of the resultant diffraction peaks produces a

pattern which is characterized of the sample. Where a mixture of different phases is present, the diffractogram is formed by addition of the individual patterns. The other uses of XRD are listed as per below:

- Measure the average spacing between layers or rows of atoms.
- Determine the orientation of a single crystal or grain.
- Find the crystal structure of an unknown material.
- Measure the size, shape and internal stress of small crystalline regions.

3.6 GANTT CHART AND MILESTONE

3.6.1 Final Year Project I

No	Detail/Week	1	2	3	4	5	6	7	Mid-semester break				8	9	10	11	12	13	14
1	Selection of Project Topic: "Carbon dioxide adsorptive removal using modified molsieve"	■																	
2	Preliminary Research Work: Research on literatures related to the topic		■																
3	Submission of Extended Proposal						●												
4	Proposal Defense																		
5	Project Work Continues: Study on the research scope and method																		
6	Submission of Progress Report																		●
7	Submission of Interim Report																		●

■ Process

● Suggested milestone

3.6.2 Final Year Project II

No	Detail/Week	1	2	3	4	5	6	7	Mid-semester break							8	9	10	11	12	13	14	15
1	Project Work Continues	■																					
2	Submission of Progress Report																						
3	Project Work Continues																						
4	Pre-EDX																						
5	Submission of Draft Report																						
6	Submission of Dissertation (soft bound)																						
7	Submission of Technical Paper																						
7	Oral Presentation																						
7	Submission of Project Dissertation (hard bound)																						

■ Process

● Suggested milestone

CHAPTER 4

RESULT AND DISCUSSION

4.1. CHARACTERIZATION

4.1.1. Fourier Transform Infrared (FTIR) Results

Transmission FTIR spectra were collected in order to investigate molecular interactions between amine-functionalized molecular sieve. Two samples were compared, which is containing unmodified molecular sieve and modified molecular sieve using monoethanolamine (MEA). Figure 4.1 and 4.2 shows the spectra of the samples in the 4000–650 cm^{-1} region. It is seen that all of the IR spectra are very similar displaying significant bands at 3300, 2920, 1630 and 960 cm^{-1} , which are associated with N-H stretch in amines, CH stretching from amine groups, NH_2 deformation of hydrogen bonded amine group and Si–O–Si(C) vibrations respectively. The broad shape of the N-H stretching bands (3300 cm^{-1}) is due to hydrogen bonding. Therefore, after amine modification, it is proven that the amine groups have been coated on the molecular sieve. The abundance of surface amine groups provides numerous chemical sites for CO_2 adsorption.

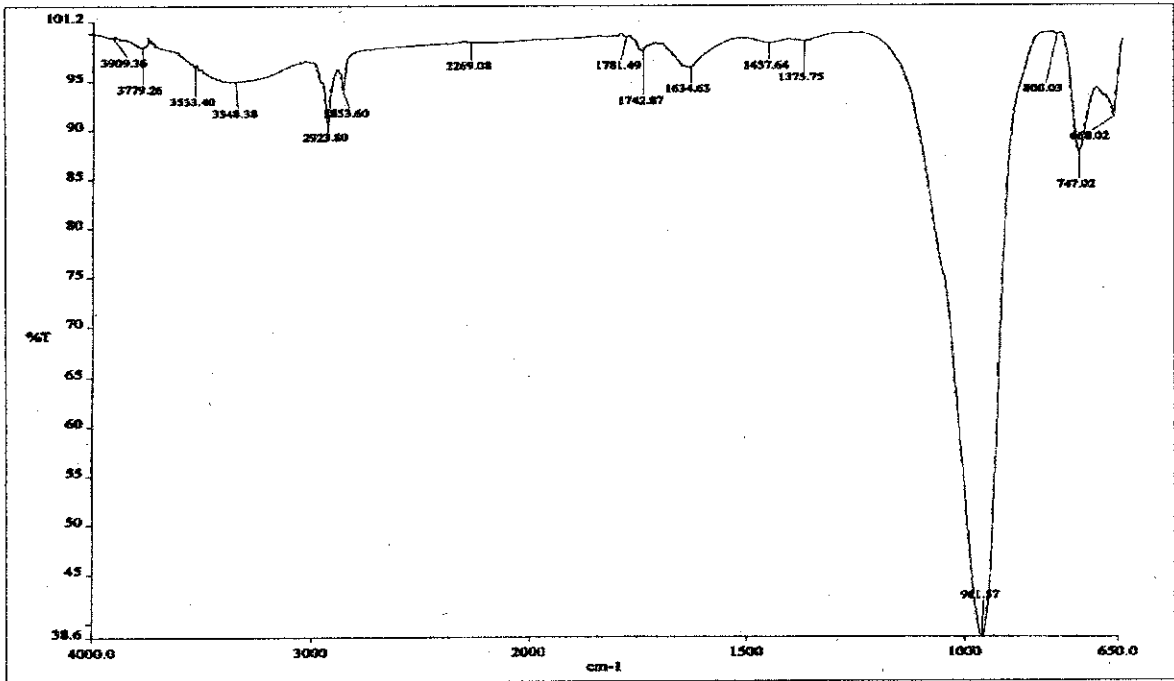


Figure 4.1: Unmodified molecular sieve

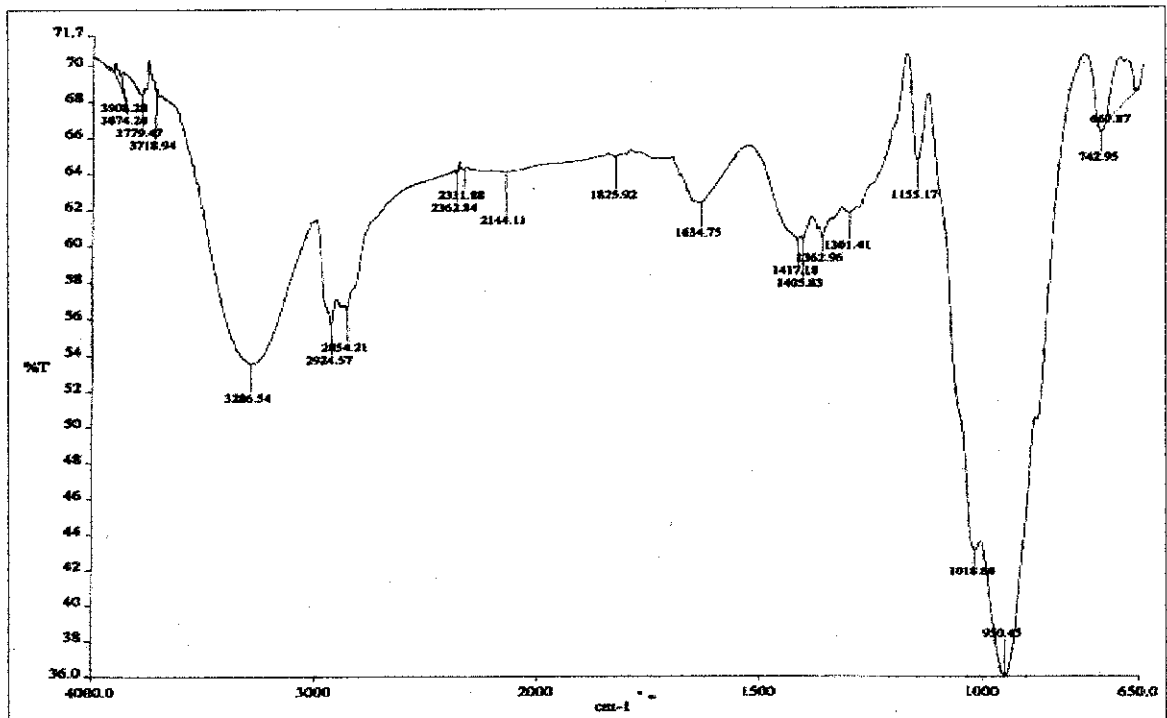


Figure 4.2: Modified molecular sieve with MEA

4.1.2 X-ray Diffraction (XRD) Results

The XRD patterns of representative two samples are shown in Figure 4.3 and 4.4. The relative peak intensity is very similar to each other for unmodified molecular sieve and modified molecular sieve with MEA. However, the relative peak intensity (478) for 6.09° of 2θ value in unmodified molecular sieve is very strong suggesting very different crystal shape. The X-ray is randomly diffracted by crystal particles and the intensity of specific peak is proportional to the exposure probability of its corresponding crystal plane. The strong peak for 6.09° of 2θ value in unmodified molecular sieve, therefore, is the result of strong and selective XRD by a particular plane of the crystal suggesting a thin plate crystal structure for unmodified molecular sieve. Apart from that, modified molecular sieve with MEA has lower intensity (316) at 6.09° of 2θ value.

There can be two possibilities that caused the lower intensity which are the effect of pore filling and the coating of outer surface of molecular sieve 13X crystals. Xu et al., (2002) reported that amine coated on the outer surface of MCM-41 crystals hardly influenced the diffraction intensity of MCM-41 support. Therefore, the low diffraction intensity of MEA/molecular sieve 13X (MEA/13X) is mainly caused by pore filling effect. Moreover, the size of MEA molecule is smaller which further verifies that it is easier for MEA molecules to fill the pores of molecular sieve 13X and resulted in lower diffraction intensity.

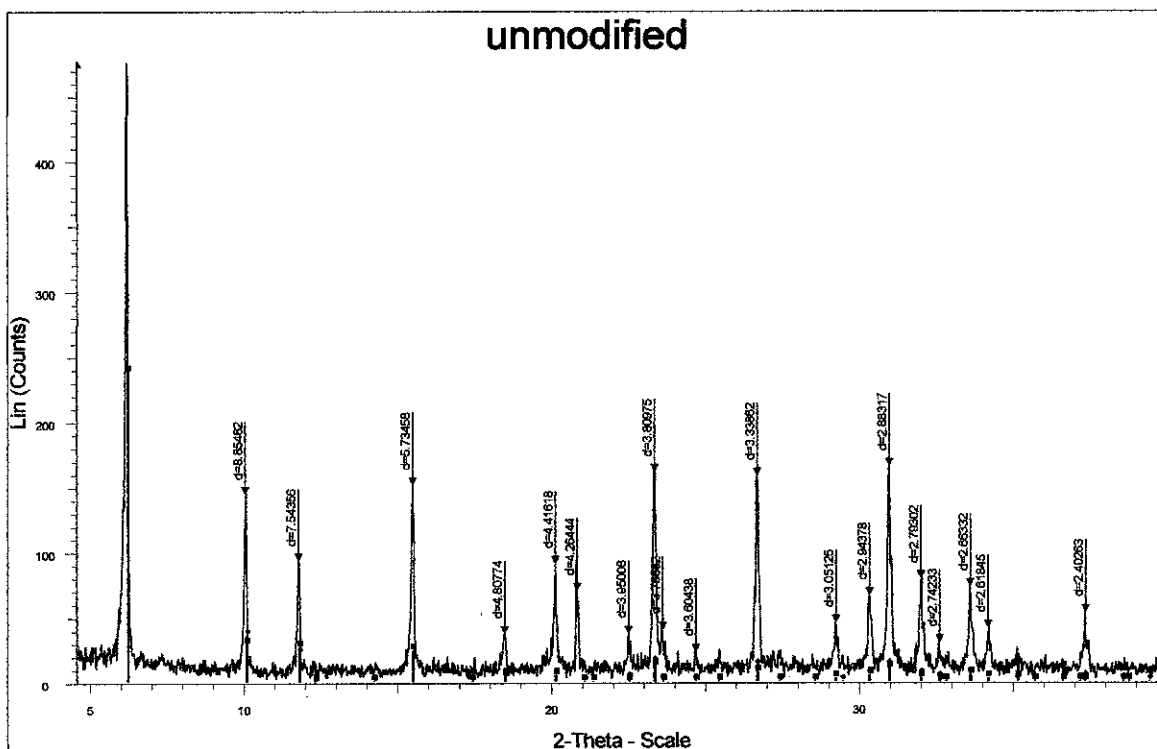


Figure 4.3: XRD pattern for unmodified molecular sieve

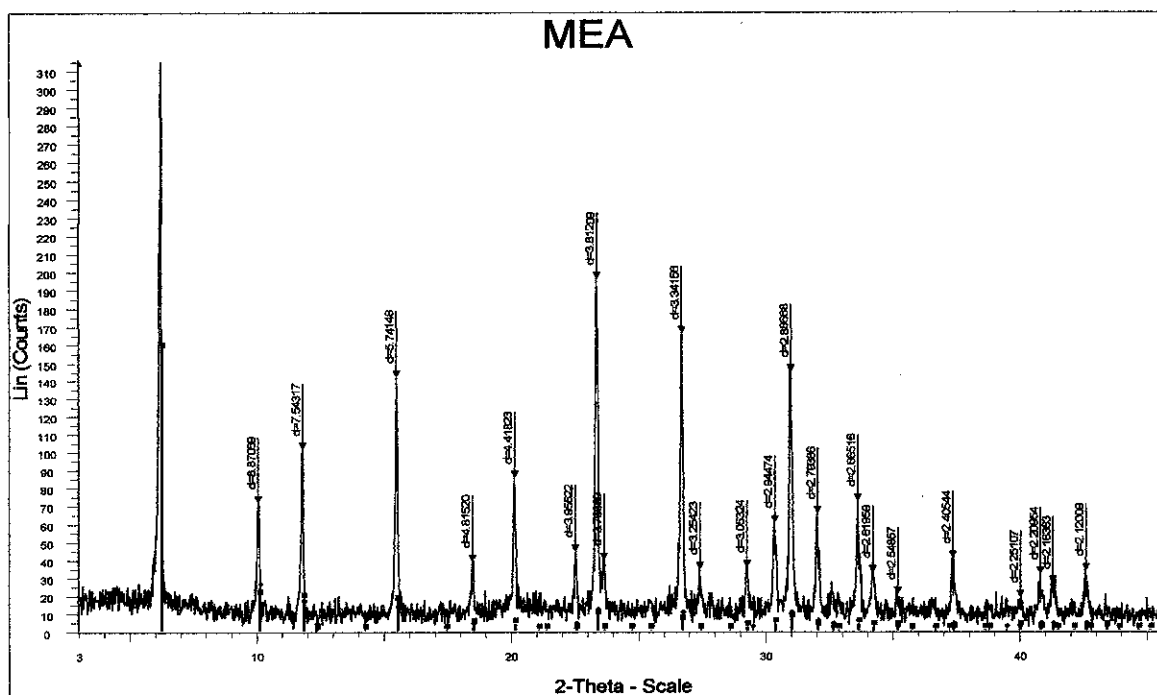


Figure 4.4: XRD pattern for modified molecular sieve with MEA

4.2. CARBON DIOXIDE SORPTION

Based upon the results obtained from the equilibrium adsorption capacity, the effects of amine modification on the CO₂ adsorption could be evaluated and characterized. In order to evaluate amine modified molecular sieve 13X as a potential material for CO₂ capture, adsorption experiment using bench scale gas reactor were carried out at 25°C, 50°C and 75°C with different pressure (10,20,30 and 40 bar). Adsorption capacity was measured until equilibrium reached.

4.2.1. Effect of Adsorption Temperature

The adsorption of CO₂ by porous materials or amines is an exothermic process. Accordingly, the adsorption capacity should decrease with the increase of temperature. The temperature has a significant effect on the adsorption capacity of the adsorbent. The CO₂ adsorption isotherm onto unmodified molecular sieve 13X (unmodified/13X) and MEA/13X were shown in figure 4.5 and 4.6. Equilibrium experiments carried out at different temperature mainly at 298,323 and 348K for a range of CO₂ pressure (10 to 40bar) were shown a decrease in the amount of CO₂ adsorbed, indicating an exothermic nature of the adsorption process. The results are evidently shown in Figure 4.5 and 4.6, as the adsorption capacity decreased when the temperature is increased.

The effects of different adsorption temperatures on CO₂ adsorption capacity for MEA/13X are presented in Figure 4.6. As expected, the CO₂ adsorption capacity at adsorption temperature 25°C (room temperature) shows the highest value at 5.67 mmol/g sorbent. When the adsorption temperature increased to 50°C, the adsorption capacity decreased to 5.53 mmol/g sorbent. When the adsorption temperature is further increased to 75°C, the adsorption capacity is the lowest at 5.40 mmol/g sorbent. These results

indicated that for each 25°C increment in adsorption temperature, about 2-3% of the adsorption capacity is reduced. At higher temperature the adsorbate CO₂ molecules tend to be in active energized form and are harder to adsorb compare to molecules at lower temperature which has lower activation energy to be adsorbed.

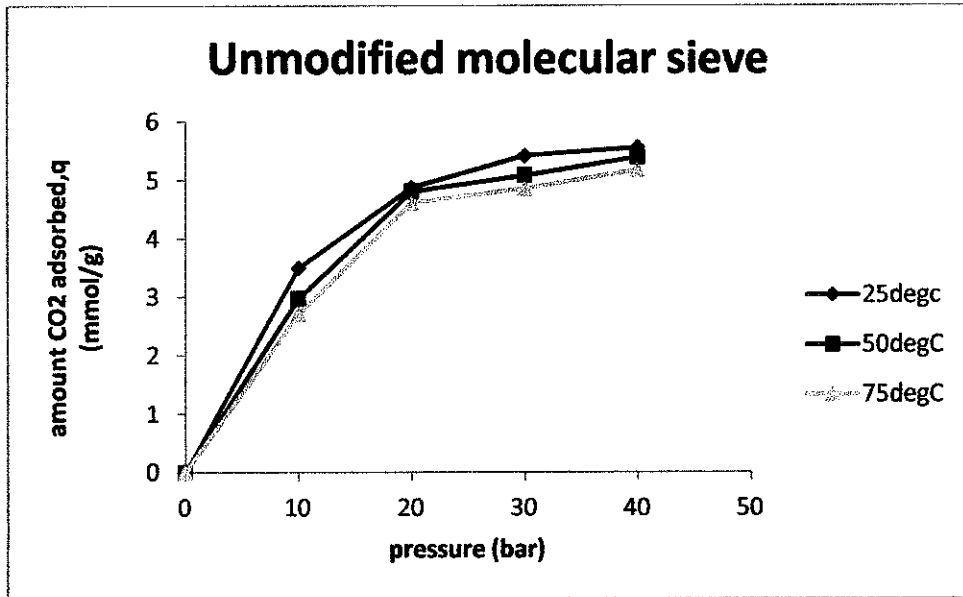


Figure 4.5: Amount CO₂ adsorbed for unmodified/13X

Table 4.1: Results for Unmodified/13X at different temperature and pressure

T = 25°C		T = 50°C		T = 75°C	
p (bar)	q(mmol/g)	p(bar)	q(mmol/g)	p(bar)	q(mmol/g)
10	3.50	10	2.97	10	2.71
20	4.87	20	4.81	20	4.62
30	5.42	30	5.08	30	4.86
40	5.55	40	5.39	40	5.18

Besides, unmodified/13X showed lower CO₂ adsorption capacity compared to MEA modified/13X. For example at 25°C (40bar) the adsorption capacity of unmodified/13X lower compared to MEA/13X which are 5.55 mmol/g sorbent and 5.67 mmol/g sorbent, respectively. It is about 2% increasing in the CO₂ adsorption capacity. This is demonstrating that CO₂ only physisorbs on this bare material while MEA/13X shows the interaction with amine groups that corresponding to a chemisorptions process. The accepted chemisorptions mechanism of CO₂ onto primary or secondary amine groups involve two steps : (a) formation zwitterions intermediate, followed by formation of carbamate as the final product under anyhydrous conditions. The reactions are illustrated in Figure 4.7.

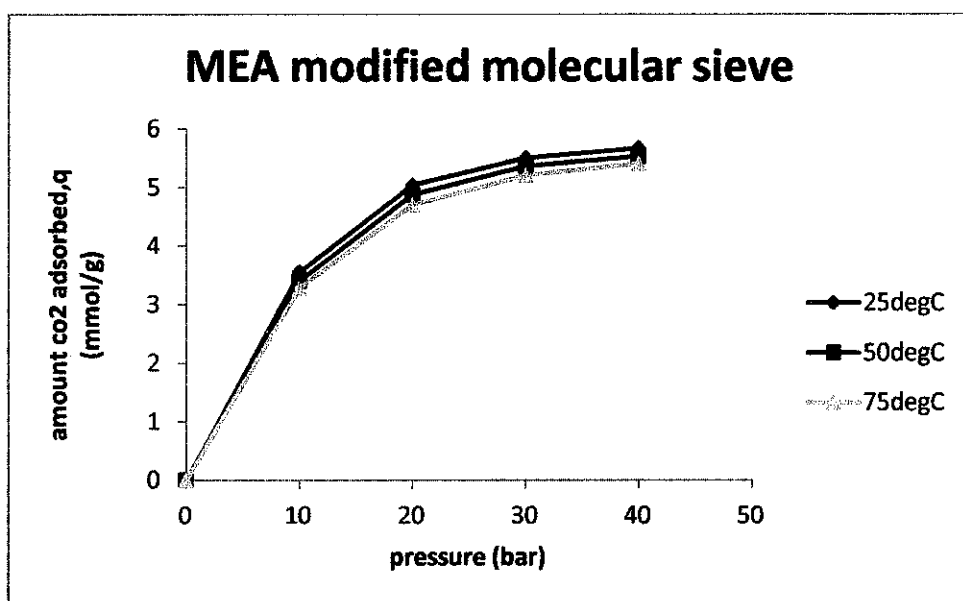


Figure 4.6: Amount CO₂ adsorbed for MEA/13X

Table 4.2: Results for MEA/13X at different temperature and pressure

T = 25°C		T = 50°C		T = 75°C	
p (bar)	q(mmol/g)	p(bar)	q(mmol/g)	p(bar)	q(mmol/g)
10	3.55	10	3.40	10	3.28
20	5.04	20	4.87	20	4.70
30	5.50	30	5.36	30	5.20
40	5.67	40	5.53	40	5.40

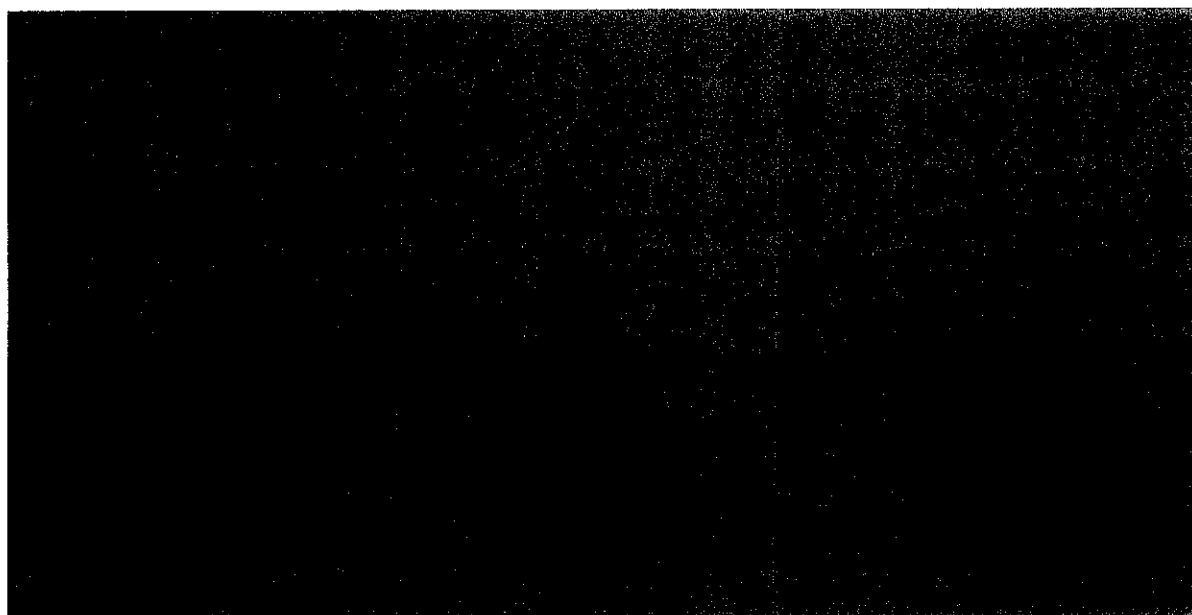


Figure 4.7: Chemisorption between primary amine bond onto molecular sieve surface and CO₂ molecules

4.2.2 Effect of Surface Density of Amines

On the other hand, CO₂ fixation on molecular sieve impregnated by the primary amine is expected to take place through the following Reaction (1) :



where, *R* is an alkyl group.

While for CO₂ adsorption on molecular sieve impregnated by the secondary amine, it follows Reaction (2) :



From Reactions (1) and (2) it can be seen that whether for the primary amine or the secondary amine, one mole of CO₂ reacts with every two moles of the primary amines or the secondary amines. Therefore, the CO₂ adsorption capacities depend on the amounts of the amino-groups: the more the amino-groups, the higher the CO₂ adsorption capacities. From the results mentioned before, it is only 2% increasing in the CO₂ adsorption capacity for MEA/13X. Thus, to have better adsorption capacities for this MEA/13X the efficiency of amine can be improved by increasing surface density of amine.

4.3. ADSORPTION ISOTHERM

For describing the adsorption equilibrium findings, different adsorption isotherm models are available. The equilibrium data were modeled using Langmuir and Freundlich model. To obtain the isotherm model parameters, the initial finding of P and q were applied in the linearized isotherm model. The regressive correlation coefficient R^2 that obtained from adsorption isotherm curves reflects the fit between the experimental data and linearized forms of isotherm models.

4.3.1. Langmuir Isotherm

This isotherm described adsorbate-adsorbent systems in which the extent of adsorbate coverage is limited to one molecular layer at or before a relative pressure of unity is reached (i.e. Type I). Although the isotherm is more usually appropriate for the description of chemisorption, the equation is nevertheless obeyed at moderately low coverages by a number of systems, and can be readily extended to describe the behaviour of binary adsorbate systems. On linearization, the equation becomes:

$$\frac{p}{q} = \frac{1}{bq_m} + \frac{p}{q_m}$$

The quantities b and q_m are treated as empirical constants. Thus the plot of p/q vs. p is linear and the slope (gradient) gives $(1/q_m)$ and the y-intercept gives $(1/bq_m)$. The curve plotted for Langmuir isotherm study for unmodified/13X and MEA/13X were shown in Figure 4.8 and 4.9.

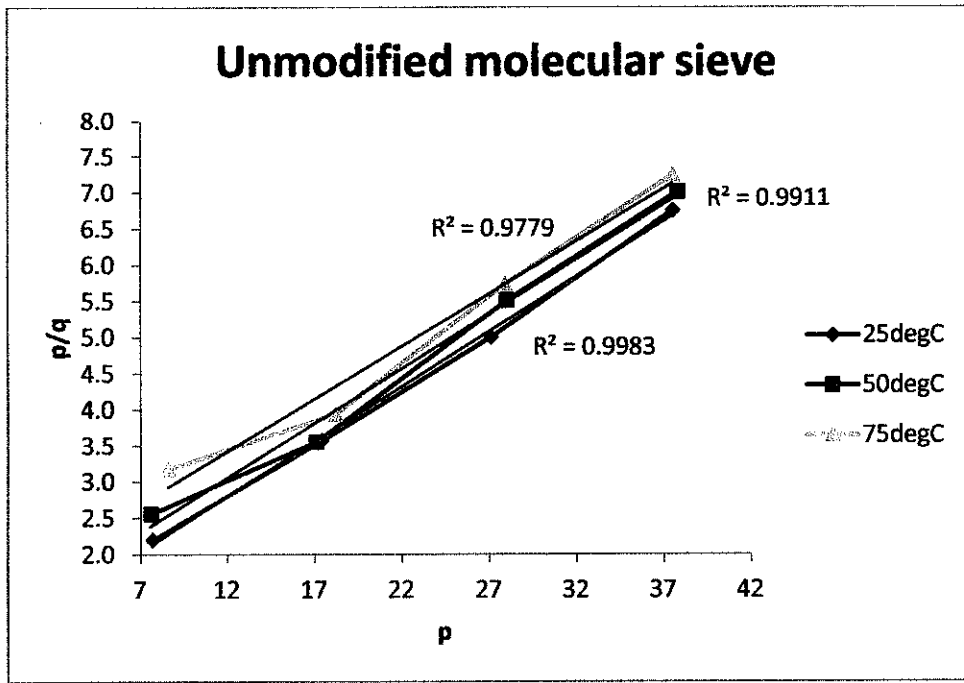


Figure 4.8: Langmuir isotherm of CO₂ onto unmodified molecular sieve at 25, 50 and 75°C

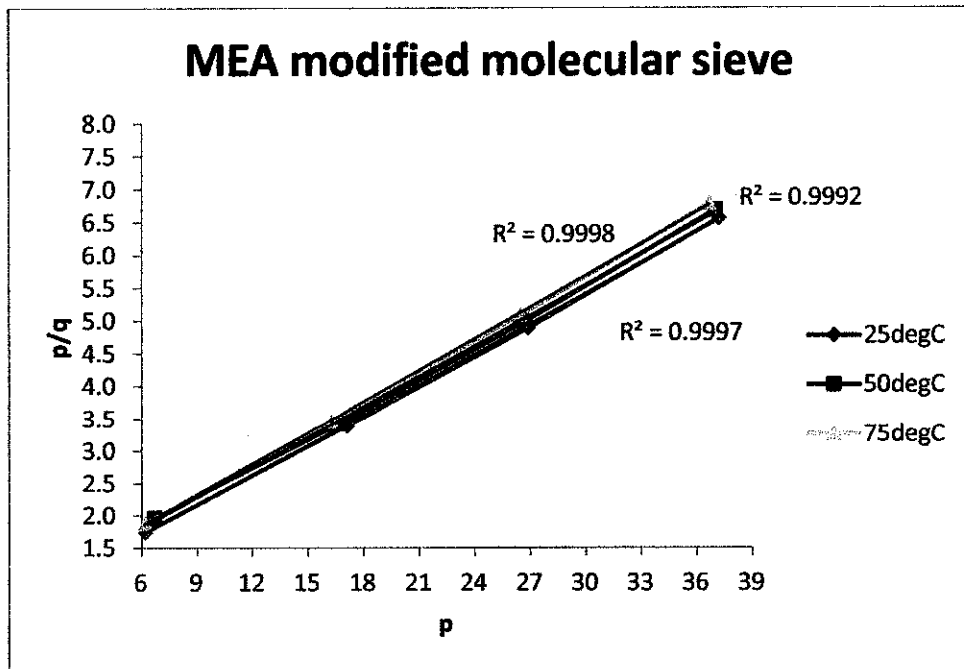


Figure 4.9: Langmuir isotherm of CO₂ onto MEA/13X at 25, 50 and 75°C

Table 4.3: R² values of Langmuir isotherm models for the adsorption of CO₂ at 25,50 and 75°C

Unmodified		MEA	
T (°C)	R ²	T (°C)	R ²
25	0.9983	25	0.9997
50	0.9911	50	0.9992
75	0.9779	75	0.9998

4.3.2. Freundlich Isotherm

The Freundlich adsorption isotherm is an adsorption isotherm, which is a curve relating the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact. The Freundlich Adsorption Isotherm is mathematically expressed as

$$\frac{x}{m} = kp^n$$

It is also written as :

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

K and n are constants for a given adsorbate and adsorbent at a particular temperature. The curves plotted for freundlich isotherm were shown in Figure 4.10 and 4.11.

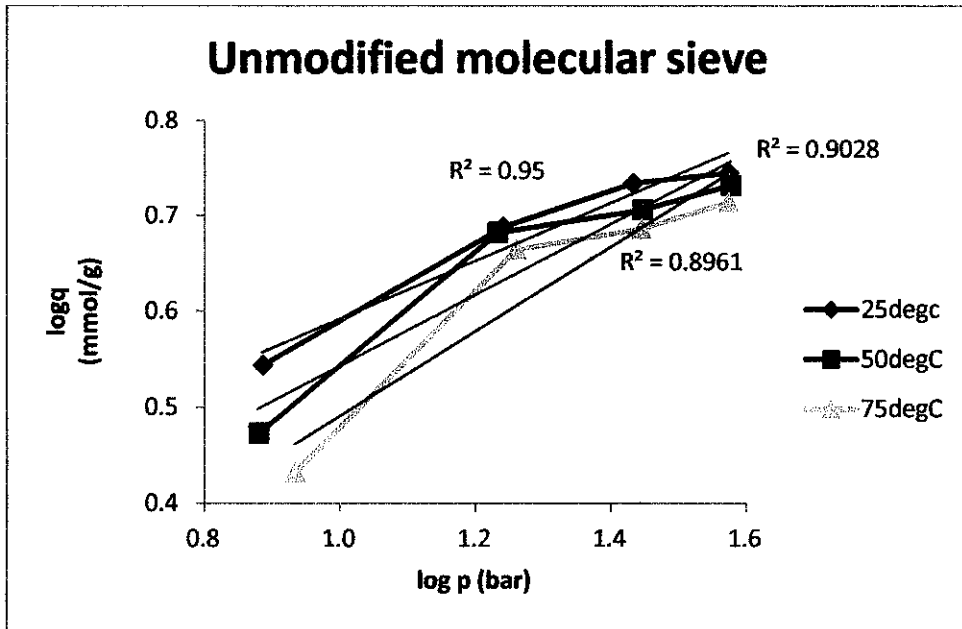


Figure 4.10: Freundlich isotherm of CO₂ onto unmodified molecular sieve at 25,50 and 75°C

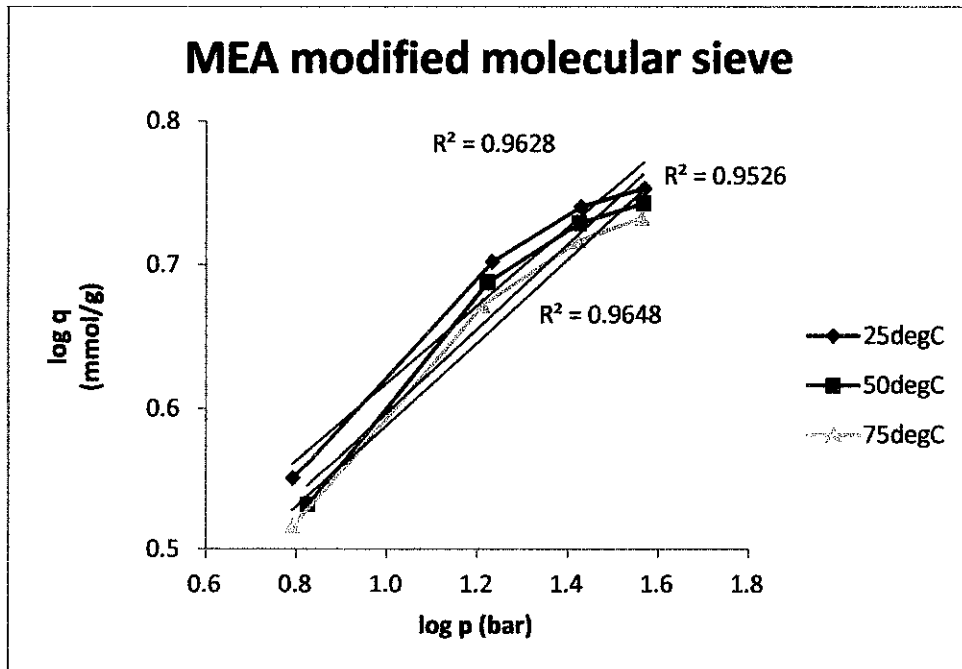


Figure 4.11: Freundlich isotherm of CO₂ onto MEA/13X at 25, 50 and 75°C

Table 4.4: R^2 values of Freundlich isotherm models for the adsorption of CO_2 at 25, 50 and 75°C

Unmodified		MEA	
T (°C)	R^2	T (°C)	R^2
25	0.9500	25	0.9628
50	0.9028	50	0.9526
75	0.8961	75	0.9648

Among these models, Langmuir model was best correlated the equilibrium data. Is is clear from Table 4.3, the regressive correlation coefficient (R^2) value for the Langmuir isotherm were high indicating a good linearity. Therefore, the Langmuir isotherm is considered as an indication for adsorption favorability.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. CONCLUSIONS

Gas adsorption characteristics of amine modified adsorbents have been successively studied in this work from the aspects of characterization, adsorption equilibrium, and adsorption isotherm. FTIR and XRD were successfully used to characterize the structure of amine modified adsorbents. The effect of pore filling and the coating of outer surface of amine modified adsorbents can be described from the intensity of XRD peak. In addition, the stretching and bending vibration of chemical bonds will further determined the integration of amines into/onto support materials.

Through this study, amine modified molecular sieve show higher adsorption capacity compared to the unmodified molecular sieve. The highest adsorption capacity was reached by MEA/13X with high CO₂ adsorption capacity at 5.67 mmol/g sobent. Thus, highest adsorption capacity can be obtained when the surface density of amine increased. The adsorption capacity will also decrease with the increasing temperature indicating the exothermic nature of adsorption process. The CO₂ adsorption capacity for MEA/13X at adsorption temperature 25°C (room temperature) shows the highest value at

5.67 mmol/g sorbent compared to 50 and 75°C which are 5.53 and 5.40 mmol/g sorbent, respectively. This is due the fact, at higher temperature the adsorbate CO₂ molecules tend to be in active energized form and are harder to adsorb compare to molecules at lower temperature which has lower activation energy to be adsorbed.

From the adsorption isotherm study, Langmuir isotherm was suitable to describe the experimental data since it results in higher regressive correlation coefficient value as per tabulated in Table 4.3, indicating a good linearity.

5.2. RECOMMENDATIONS

The following recommendations are highlighted for future work in order to obtain more understanding in gas adsorption characteristic using amine modified adsorbents. As for structural and properties characterization, Brunauer, Emmett and Teller (BET) characterization is highly recommended to obtain the pore size analysis, specific surface area, pore size distribution and percentage porosity of amine modified adsorbents. Other than that, Scanning Electron Microscope (SEM) can be used to determine the external morphology (texture), chemical composition, crystalline structure and orientation of materials by observing the high-resolution spectra from the solid samples.

Besides that, the gas adsorption process for amine modified adsorbents can be conducted using more types of amine such as Diethanolamine (DEA), Polyethyleneimine (PEI) and Diisopropylamine (DIPA) in order to gain more understanding of gas adsorption characteristics for different amine used. Meanwhile, instead of using a single pure adsorbate system, gas mixture adsorption can be carried out to further study the adsorbents selectivity properties.

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