

**CARBON DIOXIDE ADSORPTION ON EAF STEEL SLAG
DERIVED ADSORBENT**

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**CARBON DIOXIDE ADSORPTION ON EAF STEEL SLAG
DERIVED ADSORBENT**

by

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LIST OF SYMBOLS

	Symbol	Unit
W	Adsorbate loading	mg/g
c	Concentration	%
K	Adsorption constant	-
b	Constant	-
m	Constant	-
q_{abs}	Adsorption capacity	mg/g
Q	Volumetric flow rate	ml/min
ρ	Density	mg/ml
c_{CO_2}	CO ₂ concentration	%
m	mass of adsorbent	g
t_b	breakthrough time	min
c_o	Initial concentration	%

LIST OF ABBREVIATION

CO ₂	Carbon dioxide
CCS	Carbon dioxide capture and storage
PCC	Post-combustion CO ₂ capture
MEA	monoethanolamine
DEA	diethanolamine
MDEA	N-methyldiethanolamine
MCM-41	Mobil catalytic material No. 41
EAF	Electric Arc Furnace
EAFSSAD	EAF steel slag derived adsorbent
AC	Activated carbon
GAC	Granular activated carbon
EAF	Electric arc furnace
ACFs	Activated carbon fibers
BET	Brunauer-Emmet-Teller
BDDT	Brunauer, Deming, Deming and Teller
OXA-GAC	Ammonia-modified granular activated carbon
32ACSH3	Activated carbon modified by 32%NaOH using 3hrs dwelling time
PAA	Plain activated alumina

3MAA	Activated alumina modified with 30%NaOH calcined at 500°C for 4hrs
XRD	X-Ray diffraction
FTIR	Fourier Transform Infrared
SEM	Scanning electron microscope
FE-SEM	Field-emission scanning electron microscopy
EDS	Energy-dispersive spectroscopy
CMCSS	Carboxymethyl- β -cyclodextrin sodium salt
HMMM	Hexamethoxymethyl-melamine
C-700	Nitrogen enriched porous carbon which carbonization and activation at 700 °C
SBET	BET surface area

**PENGUMPULAN KARBON DIOKSIDA DENGAN PENJERAP
PENGUBAHSUAIAN PERMUKAAN PADA KARBON TERAKTIF**

ABSTRAK

Objektif kajian ini ialah menyediakan penjerap yang diperolehi daripada sanga keluli eklektik relau arka (PJSKERA), mengenalpasti kumpulan berfungsi pada penjerap dan mendapat prestasi penjerap dengan menggunakan pelbagai keadaan operasi seperti kepekatan asal CO₂, suhu penjerapan, kadar aliran gas dan muatan penjerap. PJSKERA telah disediakan dengan dua langkah. Langkah pertama ialah pengaktifan dengan natrium hidroksida dan diikuti pengurusan hidroterma. Kumpulan berfungsi pada penjerap yang disediakan telah didapati daripada FTIR. Penjerapan karbon dioksida telah dijalankan dalam system penjerapan lapisan tetap dengan penganalisis karbon dioksida dalam masa nyata untuk menentukan kepekatan karbon dioksida dalam gas keluar. Kesan-kesan keadaan operasi seperti kepekatan asal CO₂ (10 % -20 %), suhu penjerapan (30 °C -50 °C), kadar aliran gas (30 ml/min - 70 ml/min), dan muatan penjerap (1 g, 2 g, 3 g) telah dikaji. Kapasiti penjerapan tertinggi dalam kajian ini adalah 72.41 mg/g, telah diperolehi dengan menggunakan kadar aliran gas 30 mL/min, suhu penjerapan 30 °C, 10% kepekatan asal CO₂. dan 1g muatan penjerap. Kesimpulannya, keadaan operasi yang sesuai untuk penjerapan menggunakan PJSKERA ialah kepekatan asal CO₂ yang tinggi, suhu penjerapan yang rendah, kadar aliran gas yang rendah dan muatan penjerapan yang rendah.

CARBON DIOXIDE CAPTURE USING SURFACE-MODIFIED ACTIVATED CARBON ADSORBENT

ABSTRACT

The objectives of this study are to synthesis EAF steel slag derived adsorbent for CO₂ adsorption, to identify the surface functional group of prepared adsorbent by Fourier transform infrared spectroscopy (FTIR) technique and to investigate the adsorption performance of prepared adsorbent by using different parameters, initial CO₂ concentration, temperature, gas flow rate and adsorbent loading. The electric arc furnace (EAF) steel slag derived adsorbent (EAFSSAD) is prepared in two steps, NaOH activation and followed by hydrothermal treatment. The functional groups of the prepared adsorbents were characterized by FTIR. The adsorption of carbon dioxide was carried out in a fixed bed adsorption system with an online carbon dioxide analyzer to determine the concentration of carbon dioxide in the outlet gas. The effect of operating conditions such as initial CO₂ concentration (10 % - 20 %), adsorption temperature (30 °C -50 °C), gas flow rate (30 ml/min -70 mL/min) and adsorbent loading (1 g to 3 g) were studied. The highest bed adsorption capacity of EAFSSAD in this study is 72.41 mg/g with operating condition of 30 ml/min gas flow rate, 30 °C adsorption temperature, 10% initial CO₂ concentration and 1.0g adsorbent loading. In a conclusion, the suitable operating condition for adsorption of CO₂ on EAFSSAD is high initial CO₂ concentration, low gas flow rate, low adsorption temperature and low adsorbent loading.

CHAPTER ONE

INTRODUCTION

1.1 Research Background

Climate change has become one of global society's concern in term of environmental and energy policy issues in the 21st century. The increase of carbon dioxide, CO₂ emissions is considered as the main cause of the climate change (Shahkarami et al., 2015). An increase greenhouse gases in the atmosphere causes the rise in global temperature. Main emissions of CO₂ come from the combustion of fossil fuels such as coal, natural gas or petroleum, and industrial processes such as oil refinement, and the production of cement, iron and steel (Dantas et al., 2011).

The first ever scientist who published a paper about the effect of this particular human activity on Earth's climate as early as 1896 is probably Arrhenius, he estimated that coal burning would drive a rise in CO₂ concentration of about 50% in 3000 years and thought that this effect may save us from upcoming ice ages. However, after 120 years later, we are already experiencing a 50% CO₂ level increase, from 280ppm during the Industrial Revolution to 404ppm currently. This fact tells us that Arrhenius greatly underestimated the human potential. Beside, this rise in CO₂ level is correlated with increase of average temperature of Earth's surface. The rate of warming based on the period of 1979 – 2001 tends to be 0.17 K per decade (Gęsikiewicz-Puchalska et al., 2017).

The emissions of carbon dioxide into the atmosphere from the combustion of fossil fuel is recognized as a major contributor to global warming. The persistence of the petroleum economy for at least, the next two or three decades, will ensure continuous increases in atmospheric carbon dioxide level. Hence, there is a renewed urgency to develop feasible methods for the capture and long-term sequestration of carbon dioxide in geologic or oceanic reservoirs. Fossil fuel power plants has contributed approximately 30% of the gaseous CO₂

emitted into the atmosphere. The flue gases generated by these power plants are attractive candidates for the engineered capture and sequestration of CO₂ as large-scale point sources (Bai et al., 2015).

Carbon sequestration involving the carbon dioxide capture and storage (CCS) has become a major focus of reducing point-source emissions. CO₂ must be relatively pure (>95%) to find its useful applications in the fire extinguishers, metals fabrication, urea production, enhanced oil recovery, food refrigeration industry, beverage carbonation and to reduce the volume of stored CO₂ in deep saline aquifers, depleted oil and gas reservoirs and unminable coal/mineral beds (Mulgundmath et al., 2012).

Absorption, adsorption, cryogenic distillation, and membrane separation are the current or proposed methods for capturing CO₂ from flue gas. As adsorption is typically used as a final polishing step in a hybrid CO₂ capture system, solid adsorbents with high CO₂ selectivity and capacity is required in the efficient capture of CO₂ using adsorption (Bai et al., 2015).

Cryogenic CO₂ separation technology is attracting increased attention due to its significance in recent years. There are several advantages of this technology as an promising alternative to the amine scrubbing system: These advantages are to avoid the energy penalty in the regeneration process; to prevent the issue of corrosion caused by solvent; and to realize a CO₂ capture method that is environmental friendly without causing degradation (Song et al., 2013).

Besides, removing CO₂ from atmospheres with very low concentrations of CO₂ has attracted a great deal of attention. Thus, development of technologies for CO₂ separation from gases containing very low partial pressures of CO₂ is desired. CO₂ separation-based membrane is a promising candidate for realizing the air-capture strategies as it allows efficient operation at an acceptable size and cost (Moghadam et al., 2017). More and more researchers have

focused their attention on the membrane gas separation due to its increasing energy efficiency, lower cost, flexibility and environmental friendly (Zhang et al., 2017).

Chemical absorption, particularly for amine-based scrubbing technology, is preferred for post-combustion CO₂ capture (PCC) in coal-fired power plant flue gases for its high removal efficiency and scale-up feasibility (Wang et al., 2017). Alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), and N-methyldiethanolamine (MDEA) have been extensively used as amine reactive solvent. One of the key factors to the success of the capture technology is the usage of highly reactive amine (Singto et al., 2016). However, there are several problems including high regeneration energy, large equipment size, solvent degradation, equipment corrosion and high cost which accounts for about 75% of the total costs of CCS technology. Adsorption process based on solid materials has the potential to overcome those problems as an alternative to the chemical absorption process, and it takes advantages including low energy requirement, cost effective and ease of application in comparison with the chemical absorption (Zhao et al., 2012).

Adsorption is a method that has received considerable research interests in the last decade. Activated alumina, activated carbon, mesoporous carbons, carbon fiber, carbon nanotubes, mobil catalytic material No.41 (MCM-41), TiO₂ nanotubes, and zeolite are potential adsorbents for CO₂ capture from mixed gases. Among these, activated carbon offers an attractive and relatively inexpensive adsorbent for CO₂ separation (Kongnoo et al., 2016).

There is another issue that creates the environmental problem which is the waste generated from the industrial production of metals. The increasing production of metals increase the amount of waste generated. The generated waste become an environmental problem that must be dealt with. It is essential to make these materials as resources to be utilized in other industries in the future (Etxeberria et al., 2010).

Steel slag is one of the main by-products of the metallurgical industry. Currently, steel production is basically sub-divided into two manufacturing processes which are integral siderurgy and the electric cycle. Pig iron is melted in a Blast Furnace (BF) and then converted into steel in a Basic Oxygen Furnace (BOF) in integral siderurgy while the electric cycle mainly involves melting recycled scrap in the Electric Arc Furnace (EAF). Then, the steel can be processed into high-grade steels either by refining in either a Ladle Furnace (LF) or in specific converters for high-alloy steel or stainless steel (Skaf et al., 2017).

1.2 Problem Statement

The rise in CO₂ level has been recognized as one of the contributor in climate change, a problems that need urgent solution. The current technology used for post combustion CO₂ capture is by using liquid absorption using amines which have drawbacks of high regeneration energy, large equipment size, solvent degradation, equipment corrosion and high cost. Another problem addressed here is the waste generated from metallurgical industry also creates environmental problem. The synthesis of EAF steel slag derived adsorbent (EAFSSAD) for solid adsorption of carbon dioxide is proposed in this study to solve these problems. By preparing the EAFSSAD, the cost of synthesis of adsorbent is reduced and also the waste of metallurgic industries, electric arc furnace (EAF) steel slag is utilized. The coconut shell is used as the precursor of the adsorbent.

1.3 Research Objectives

The objectives are to:

- a) prepare EAF steel slag derived adsorbent (EAFSSAD) for CO₂ adsorption
- b) identify the surface functional group of prepared adsorbent by Fourier transform infrared spectroscopy (FTIR) technique.
- c) investigate the adsorption performance of prepared adsorbent.

1.4 Scope of Study

The scope of study of this study includes the synthesis of EAF steel slag derived adsorbent (EAFSSAD), characterization of prepared adsorbent, study of adsorption process parameters of the EAFSSAD in the CO₂ adsorption using a fixed-bed adsorption system. Commercially available coconut shell was selected to be used to enhance the surface area and porosities of the EAFSSAD. The EAFSSAD was prepared from coconut shell and EAF steel slag in two steps, namely sodium hydroxide (NaOH) activation followed by hydrothermal treatment.

The synthesized adsorbent was characterized by using FTIR analysis. The functional groups of the fresh sample were determined. Furthermore, the functional groups of used sample were characterized by FTIR analysis to compare with the result of fresh sample.

A fabricated fixed-bed adsorption system with an online CO₂ analyzer was used to determine the CO₂ adsorption performance of the prepared adsorbents. The effect of operating condition parameters such as initial CO₂ concentration, adsorption temperature, gas flow rate and adsorbent loading were studied in order to obtain the best condition for CO₂ adsorption. Finally, the results will help to find out the CO₂ adsorption performance of the prepared adsorbents and figure out the optimum condition for CO₂ adsorption.

1.5 Organization of thesis

This thesis consists of five chapters. Chapter one (Introduction) presents the current environmental issues and different approach to reduce CO₂ level on the earth. It also presents the problem statement and the research objectives.

Chapter two (Literature reviews) describes the adsorption process and the theory of adsorption. Different adsorption isotherm had been studied as well. This chapter also studied different adsorbents to capture CO₂ and their adsorption performances. The effect of operating parameters using different adsorbents was discussed.

Chapter three (Materials and methods) shows the outline of experimental works in this research. This chapter is divided into three parts. The materials and equipment used are listed in the first and second part. In the third part, the method of preparation for EAFSSAD is described in details. The procedures for CO₂ adsorption study, the calculations of adsorption capacity are also included in this part.

Chapter four (Results and discussion) presents all the results and discussions on the findings. This chapter is divided into two parts. Part one is the results of characterization while part two shows the adsorption performances of EAFSSAD with different operating conditions.

Finally, chapter five (Conclusions and recommendations) summarizes the data reported. This chapter also provides some recommendations for future research.

CHAPTER TWO

LITERATURE REVIEW

2.1 Adsorption

The process of adsorption occurs due to the presence of unbalanced or residual forces at the surface of an adsorbent, forming a molecular or atomic film (adsorbate). Adsorption is a surface phenomenon. Adsorption can be classified into physisorption and chemisorption based on the nature of forces involved. When the force of attraction existing between adsorbate and adsorbents are weak Van der Waals forces, then the process is known as physisorption. Physisorption takes place with formation of multilayer of adsorbate on adsorbent.

When the forces of attraction existing between adsorbate and adsorbent are through the formation of strong chemical or ionic bond, the process is known as chemisorption. Chemisorption occurs with formation of unilayer of adsorbate on adsorbent. It involves the substantial rearrangement of electron density and due to the transformation of components in a chemical form, it is therefore irreversible. Additionally, this process can be influenced by several factors such as the interactions between adsorbate and adsorbent, nature of adsorbate, the surface area and pores structure of adsorbent, operating temperature and contact time.

Most adsorbents used in the adsorption are highly porous material. Adsorption normally takes place on the walls of the pores or at specific sites inside the particle. The pores generally are very small, thus the internal surface area are greater than the external area and is often 500 to 1000 m²/g (McCabe et al., 2005). Separation is occurred due to the differences in molecular weight, shape or polarity cause some molecules to be held more strongly on the surface than others or because the pores are too small to admit the larger molecules. Normally, the adsorbing component (or adsorbate) is held strongly enough to permit complete removal of that component from the fluid with very little adsorption of other components. Regeneration of the

adsorbents can then be carried out to obtain the adsorbate in concentrated or nearly pure form (McCabe et al., 2005).

2.2 Types of Adsorption Isotherms

Some typical isotherm shapes are shown as arithmetic graphs in the Figure 2.1 (McCabe et al., 2005). The linear isotherm goes through the origin, the amount adsorbed is proportional to the concentration in the fluid. Isotherms that are convex upward are called favourable, because a relatively high solid loading even at low concentration in the fluid. The Langmuir isotherm (McCabe et al., 2005) is given by the following equation:

$$W = W_{max} \left[\frac{Kc}{1+Kc} \right] \quad (2.1)$$

where,

W = adsorbate loading, mg/g

c = concentration of the fluid, ppm

K = adsorption constant,

This isotherm is of the favourable type. When K is large and $Kc \gg 1$, the isotherm is strongly favourable; when $Kc < 1$, the isotherm is nearly linear. The Langmuir isotherm is derived assuming a uniform surface, however it is not a valid isotherm but the relation applies fairly well for gases which are weakly adsorbed.

The empirical Freundlich equation is suitable for the strongly favourable isotherms. The equation is given below:

$$W = bc^m \quad (2.2)$$

where,

W = adsorbate loading, mg/g

$b = \text{constant}$,

$m = \text{constant}$.

when $m < 1$, it is often a better fit, particularly for adsorption from liquids.

Irreversible isotherm is the very limiting case of a very favourable isotherm, where the amount adsorbed is independent of the concentration down to very low value. All systems show a decrease in the amount adsorbed with an increase in temperature. However, adsorbate can be removed by raising the temperature even for the cases labelled “irreversible”. Unfortunately, desorption requires a much higher temperature when the adsorption is strongly favourable or irreversible than when the isotherms are linear (McCabe et al., 2005).

Unfavourable isotherm is the isotherm that concave upward because relatively low solid loadings are obtained and it leads to long mass-transfer zones in the bed. Isotherms of this shapes are rare, but they are worth studying to help understand the regeneration process. If the adsorption isotherm is favourable, mass transfer from the solid back to the fluid phase has characteristics similar to those for adsorption with unfavourable isotherm (McCabe et al., 2005).

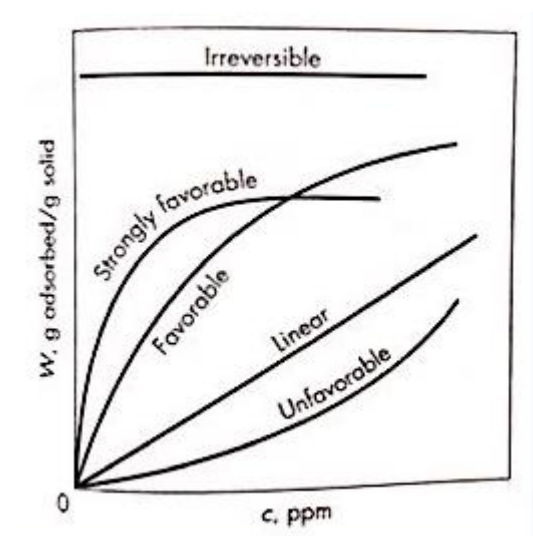


Figure 2-1 : Adsorption Isotherms (McCabe et al., 2005).

2.3 Different adsorbent used to capture CO₂

According to the study by Bai et al. (2015), activated carbon fibers (ACFs) with controlled pore sizes were prepared by potassium hydroxide (KOH) activation for adsorption of CO₂. Hydrofluoric acid is used to modify the surfaces of the ACFs in order to enhance the adsorption of CO₂ by the fibers based on the effects of the oxygen-containing functional groups introduced on the surface. Oxygen-containing functional groups were effectively introduced onto the surfaces of the ACFs based on the fluorine radical effect. The surface oxygen complexes of porous carbon materials effectively provide electron-rich properties, which can enhance their interaction with the surface of carbon adsorbents and CO₂ due to the introduction of various polar groups, such as hydroxyl (OH) and carboxyl (COOH) groups. Overall, the CO₂ uptakes of the samples were 0.76 (R-ACF), 1.39 (1M-ACF), 1.42 (2M-ACF) and 1.61 mol/kg (4M-ACF) (Bai et al., 2015). The adsorption amounts of CO₂ on the liquid-oxidized ACFs were greater than those observed for the R-ACF sample, particularly the 4M-ACF sample. Thus, this proved that the introduction of carboxylic and hydroxyl surface groups effectively improving the CO₂ adsorption behaviour (Bai et al., 2015).

In another study by Zhao et al. (2012), polyacrylamide-impregnated silica gel was prepared to capture CO₂ from flue gas. The polymerization of acrylamide was carried out in acetonitrile solvent using azodiisobutyronitrile as initiator and ethylene glycol dimethacrylate as crosslinker. The polymer was not only occupying the porosity of the silica, but necessarily surrounding silica particles, and the amide groups was successfully loaded on the support silica. The CO₂ adsorption isotherms were measured to examine CO₂ adsorption on adsorbents, and the results showed the significant increase in the adsorption capacity after modification. In this study, silica gel (silica), impregnated silica (AAM-silica), and polyacrylamide (poly-AAM) were used as adsorbents. Based on the CO₂ adsorption isotherms at 333 K, the adsorption capacity is 0.220 mmol g⁻¹ for silica, 0.637 mmol g⁻¹ for AAM-silica, and 0.475 mmol g⁻¹ for

poly-AAM (Zhao et al., 2012). The CO₂ amounts adsorbed for AAM-silica is obviously greater than that for silica, which may be associated with the amide activated sites on silica after impregnation, providing strong attraction to CO₂ (Zhao et al., 2012).

In the study by Shafeeyan et al. (2015), commercial granular activated carbon (GAC) and an ammonia-modified GAC (OXA-GAC) were used as adsorbents. The isotherms of both adsorbents are of Type I according to BDDT (Brunauer, Deming, Deming and Teller) Classification (Do and Wang, 1998), indicating that the pore structure of the carbon samples is mainly composed of a well developed micropore volumes. It was assumed that the adsorption of untreated GAC only involved physisorption while the OXA-GAC involved both physisorption and chemisorption. Chemisorption is the occurrence of strong chemical reaction of CO₂ and incorporated nitrogen-functionalities on the surface in this study. We found out that the OXA-GAC adsorbent exhibited a higher CO₂ uptake, especially at low partial pressures.

According to the study by Tan et al. (2014), the adsorbents used is the unmodified granular coconut shell activated carbon (unmodified AC) and sodium hydroxide-modified granular coconut shell activated carbon. The activated carbon modified by 32% sodium hydroxide using 3 hours dwelling time shows the best adsorption capacity over other NaOH concentrations and dwelling times, the modified adsorbents is known as 32ACSH3. The surface of the 32ACSH3 contains some N₂ functional groups, which may be responsible for the CO₂ adsorption at low temperature. Moreover, the presence of sodium molecules on the surface of 32ACSH3 might absorb CO₂ and form Na₂CO₃ at low temperature, however when the temperature increases, then Na₂CO₃ will decompose and convert into CO₂ and H₂O, which greatly reduce the CO₂ adsorption. In this study, the unmodified AC (without NaOH loading) can adsorb 17.52 mg/g CO₂, while the 32ACSH3 can adsorb 27.10 mg/g CO₂ (Tan et al., 2014).

In the study of Auta et al. (2013), a cost effective, low energy intensity, environmental friendly and high capacity adsorbent from activated alumina for CO₂ adsorption was developed. The adsorbent used were plain activated alumina (PAA) and optimally modified adsorbent with 30% NaOH calcined at 500 °C for 4 h (3MAA) were used as adsorbent for the capture of CO₂. Modification of the activated alumina with 30 % NaOH (3MAA) was observed to have reduced the surface area of the activated alumina from 207.14 to 203.32 m²/g occurred which was attributed to structural changes of the adsorbent according to the X-ray diffraction (XRD) results (Auta et al., 2013). However, the structural changes after modification increased the total pore volume and average pore width. Adsorption capacity of 3MAA and PAA were 51.92 and 19.61 mg/g even with their surface areas of 203 and 207 m²/g, respectively (Auta et al., 2013). The enhanced adsorption on 3MAA was due to its average pore width and total pore volume which were larger than those of PAA. Besides, modification of the activated alumina with sodium hydroxide introduced some molecules of sodium on its surface which enhanced formation of sodium carbonate as CO₂ was adsorbed (Auta et al., 2013).

According to the study by Auta and Hameed (2014), the mesoporous activated alumina functionalized with diethanolamine (DEA) was used for selective adsorption of carbon dioxide (CO₂) from its mixture with nitrogen gas. The BET textural analysis revealed a pore size and surface area of 5.3 nm and 205 m²/g for DEA as compared with 5.7 nm and 207 m²/g, respectively of the plain activated alumina reported in their previous work (Auta et al., 2013). However, a total pore volume of 0.39 nm for DEA was obtained which showed an enhancement after functionalization. Dissolution of the DEA wall during functionalization may have caused the expansion or structural changes due to reaction between the diethanolamine. The porosity of the DEA enhanced physical adsorption while, the numerous amine groups on its surface (revealed by the Fourier Transform Infrared (FTIR) spectrum) promoted chemical interaction with the CO₂ molecules. The effect of the gas mixture feed flow rate, column adsorption

temperature, DEA bed height and concentration of CO₂ in the feed stream was studied and showed that 90 mL/min, 35°C, 3 g and 10% of CO₂, respectively were the optimum operating conditions for the highest adsorption capacity of 55.94 mg/g (Auta and Hameed, 2014).

According to the study by Guo et al. (2017), carboxymethyl- β -cyclodextrin sodium salt (CMCSS) was synthesized as an adsorbent for CO₂ capture. Compared with β -cyclodextrin, CO₂ adsorption capacity of CMCSS was obviously improved at low temperatures (e.g. 298 K) due to the alkalization and etherification. This study found an interesting and unique behaviour of CMCSS, the CO₂ adsorption capacity on CMCSS increased with the increase of temperature at CO₂ pressure above 1.2 bar; and the increase was also observed with the increase of pressure. For instance, CO₂ adsorption capacity at 3.5 bar increased from 0.46 mmol/g at 298 K to 0.91 mmol/g at 403 K. Besides, the difference of CO₂ adsorption capacities between 298 and 403 K was changed from 0.13 mmol/g at 2 bar to 0.45 mmol/g at 3.5 bar, showing that CO₂ capture can be improved by pressure rising in a pressure swing adsorption (PSA) process (Guo et al., 2017). This study draw a conclusion that the CO₂ adsorption capacity on the adsorbent was not sensitive to temperature at low pressure, but increased with the increasing of temperature at high pressure (Guo et al., 2017).

In the study by Goel et al. (2016b), nitrogen enriched porous carbons were used for the CO₂ adsorption. Carbonization and activation at 700 °C using hexamethoxymethyl-melamine (HMMM) as precursor and MCM-41 silica as template. produced carbon with highest surface area of 463 m²/g and total pore volume of 0.48 cm³/g with nitrogen content of 9.2 wt% (Goel et al., 2016b). This adsorbent was denoted as C-700. As carbonization temperature increases, BET surface area (SBET) of the synthesized carbon materials increases and reach a maximum for sample carbonized at 700 °C. Further increase in carbonization temperature to 800 °C greatly decreased (around 75%) the BET surface area and total pore volume. This adsorbent shows highest CO₂ uptake of 0.80 mmol/g at 30 °C using pure CO₂.(Goel et al., 2016b).

2.4 Factors affecting the adsorption capacity of adsorbents on CO₂

2.4.1 Temperature

The comparison of adsorbents at different adsorption temperature was shown in the Table 2.1. Based on the Table 2.1, it can be observed that the higher the temperature, the lower the adsorption capacity. The adsorption capacity of Polyacrylamide-impregnated silica gel decreased as temperature increased maybe a consequence of exothermic nature of adsorption process, where both the molecular diffusion rate and the surface adsorption energy increase with increasing temperature (Shafeeyan et al., 2015). This trend of lower adsorption capacity with high temperature indicates that the adsorption of CO₂ is physisorption (Tan et al., 2014).

2.4.2 Gas Flow Rate

The comparison of adsorbents at different gas flow rate was shown in the Table 2.1. Based on the Table 2.1, it can be observed that the higher the gas flow rate, the lower the adsorption capacity. The breakthrough time at slow flow rate was more than breakthrough time at high flow rate, this is due to the longer residence time experienced at slower flow rate, allow the diffusion of CO₂ molecules, resulted in higher adsorption capacity (Auta et al., 2013). Early saturation of adsorption column adsorbent bed was associated with higher mass transfer coefficient emanating from high flow rate (Auta et al., 2013).

2.4.3 Initial CO₂ Concentration

The comparison of adsorbents at different CO₂ concentration was shown in the Table 2.1. Based on the Table 2.1, it can be observed that the higher the CO₂ concentration, the higher the adsorption capacity. Increase in percentage of CO₂ in the feed increased the concentration gradient. Other researchers found that the concentration gradient can overcome the mass transfer resistance as well as increasing the adsorption capacity (Chen et al., 2011). However, NaOH modified activated alumina did not follow the trend. The adsorption capacity increase

at first, but decrease at 18% CO₂ concentration due to the outrageous inflow of CO₂ molecules (18%) outstripped the limited available active sites on the adsorbent surface (Auta et al., 2013).

2.4.4 Adsorbent Loading

The comparison of adsorbents at different adsorbent loadings was shown in the Table 2.1. Based on the Table 2.1, it can be observed that the higher the adsorbents loading, the higher the adsorption capacity. An increase in the amount of adsorbent was accompanied with subsequent increase in the service area of the adsorbent. The service area increase enhanced more contact between the active sites on the adsorbents and CO₂ molecules, thus increasing the adsorption capacity. It is also interesting to note that enlarged service area increased the volume of synthetic flue gas (CO₂/N₂ mixture) treatment as well as gave a prolonged breakthrough point attainment (Auta et al., 2013). However, adsorption using NaOH-modified activated carbon (32ACSH3) shows an opposite trend, the greater the amount of adsorbent loadings, the lower the adsorption capacity. Increasing the adsorbent loading did not increase the adsorption capacity of CO₂. The highest adsorption capacity of 27.01 mg/g was found for the lowest 32ACSH3 loading of 3 g. The higher adsorbent loading means higher total surface area of 32ACSH3, but fewer CO₂ molecules were adsorbed onto the surface per gram unit of 32ACSH3, which led to lower adsorption capacity at high adsorbent loading (Tan et al., 2014).

Figure 2-2 shows the breakthrough curve of CO₂ adsorption at different adsorption temperature, different gas flow rate and different initial CO₂ concentration. From Figure 2.2, it can be observed that generally, the breakthrough time become faster with increasing temperature. Besides, it also can be observed that the higher the gas flow rate, the shorter the breakthrough time .and the higher the initial CO₂ concentration, the shorter the breakthrough time.

Table 2.1: Comparison of adsorbents at different operating condition

Adsorbents	Adsorption Temperature (K)	Gas flow rate (ml/min)	Initial concentration (%)	CO₂	Adsorbent loadings (g)	Adsorption Capacity (mmol/g)	References
Polyacrylamide-impregnated silica gel	318	170	13		2.5	0.78	Zhao et al. (2012)
	333	170	13		2.5	0.57	
	348	170	13		2.5	0.49	
	363	170	13		2.5	0.43	
	333	130	13		2.5	0.68	
	333	170	13		2.5	0.57	
	333	210	13		2.5	0.51	
	333	170	5		2.5	0.45	
	333	170	9		2.5	0.53	
	333	170	13		2.5	0.57	
	333	170	17		2.5	0.62	
OXA-GAC	303	-	-		-	1.71	Shafeeyan et al. (2015)
	333	-	-		-	1.12	

Table 2-1 continue

Adsorbents	Adsorption Temperature (K)	Gas flow rate (ml/min)	Initial CO₂ concentration (%)	Adsorbent loadings (g)	Adsorption Capacity (mmol/g)	References
NaOH modified-activated carbon	308	90	10	3.0	0.62	Tan et al. (2014)
	318	90	10	3.0	0.55	
	328	90	10	3.0	0.36	
	308	120	10	3.0	0.58	
	308	150	10	3.0	0.58	
	308	90	15	3.0	0.67	
	308	90	20	3.0	0.78	
	308	90	10	4.5	0.39	
	308	90	10	6.0	0.32	
NaOH modified-activated alumina	308	90	15	4	1.18	Auta et al. (2013)
	318	90	15	4	0.77	
	328	90	15	4	0.73	
	308	120	15	4	0.91	
	308	150	15	4	0.86	

Table 2-1 continue

Adsorbents	Adsorption Temperature (K)	Gas flow rate (ml/min)	Initial concentration (%)	CO₂	Adsorbent loadings (g)	Adsorption Capacity (mmol/g)	References
NaOH modified-activated alumina	308	90	12		4	0.56	Auta et al. (2013)
	308	90	18		4	0.75	
	308	90	15		2	0.83	
	308	90	15		6	1.25	
Diethanolamine activated alumina	308	90	10		3	1.27	Auta and Hameed (2014)
	318	90	10		3	0.72	
	328	90	10		3	0.60	
	308	120	10		3	0.89	
	308	150	10		3	0.61	
	308	90	15		3	1.46	
	308	90	20		3	1.60	

Table 2-1 continue

Adsorbents	Adsorption Temperature (K)	Gas flow rate (ml/min)	Initial concentration (%)	CO₂	Adsorbent loadings (g)	Adsorption Capacity (mmol/g)	References
Diethanolamine activated alumina	308	90	10		2	0.66	Auta and Hameed (2014)
	308	90	10		4	1.53	
Nitrogen enriched porous carbons which prepared at 700 °C	303	50	10		0.02	0.531	Goel et al. (2016b)
	323	50	10		0.02	0.262	
	348	50	10		0.02	0.212	
	373	50	10		0.02	0.112	
	303	50	20		0.02	0.621	
	303	50	50		0.02	0.714	
303	50	100		0.02	0.800		

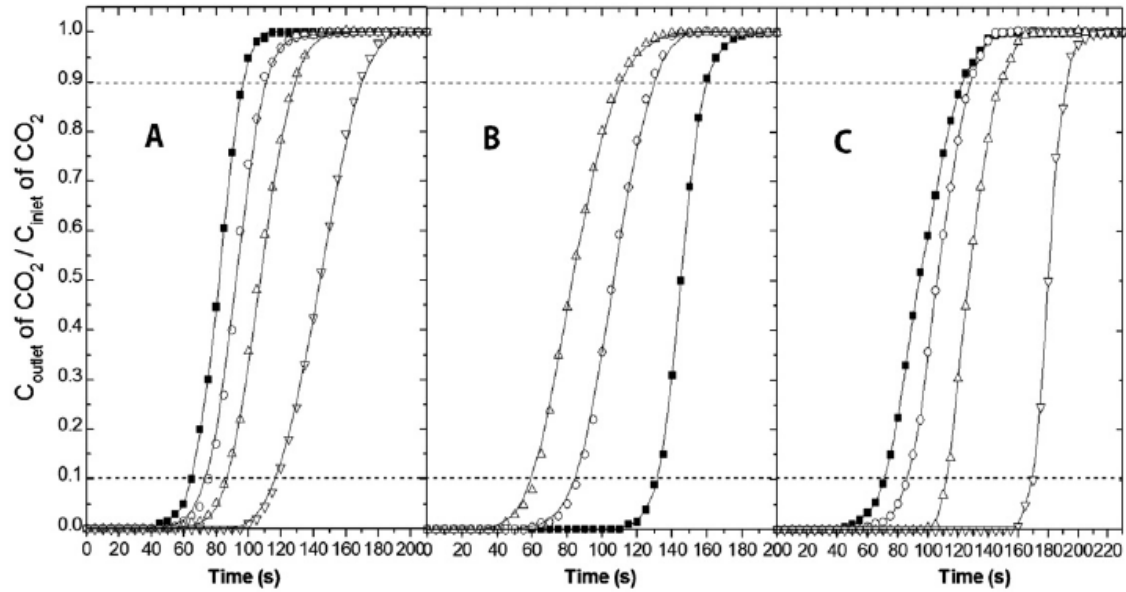


Figure 2-2 : Breakthrough curve at different operating condition (Zhao et al., 2012).

Experimental (scatters) and predicted (solid lines) breakthrough curves of CO₂.

(A) Breakthrough curve of CO₂ at 318 K (∇), 333 K (\triangle), 348 K (\blacksquare) and 363 K (\circ) respectively, the feed CO₂ concentration and flow rate were 13% and 170 ml/min. (B) Breakthrough curves of CO₂ at flow rate of 210 ml/min (\triangle), 170 ml/min (\circ), and 130 ml/min (\blacksquare) respectively, the temperature and feed CO₂ concentration were set as 333K and 13%. (C) Breakthrough curves of CO₂ under feed CO₂ concentration of 17% (\blacksquare), 13% (\circ), 9% (\triangle) and 5% (∇) respectively, the temperature and flow rate were set at 333 K and 170 ml/min.

2.5 Electric Arc Furnace (EAF) Steel Slag and Zeolite

As the industrial production of metals increases, the amount of waste generated become an environmental problem that must be dealt with. Thus, it is good to use this materials as resources to be utilized in other industries in the future. Steel slag is one of the main by-products of the metallurgical industry. In terms of chemical composition, the EAF slag is mainly consisted of iron oxides (FeO, Fe₂O₃, Fe₃O₄), lime (CaO), silica (SiO₂), magnesia (MgO) and

alumina (Al_2O_3) (Ter Teo et al., 2016 ; Skaf et al., 2017). These chemical composition made it suitable as the precursor of zeolite. Zeolites are nano-porous inorganic materials that are used in various important applications such as catalysis, ion exchange and separations. Zeolites are crystalline microporous aluminosilicates with a structure based on a three-dimensional network of aluminium and silicon tetrahedra linked by oxygen atoms (Kongnoo et al., 2017). The zeolites are usually synthesized from different sources of silica and alumina by hydrothermal treatment in order to reduce the cost of synthetic zeolites (Garshasbi et al., 2017). Zeolites have the potential for a wide range of applications, for example, as adsorbents, molecular sieves or catalysts due to their large specific surface area, specific pore sizes, molecular sieving ability and acidity. Zeolites also have high carbon dioxide (CO_2) adsorption capacity and good desorption characteristics (Kongnoo et al., 2017).

2.6 Activated Carbon

Activated carbon (AC) is a carbonaceous, highly porous adsorptive medium that has a complex structure composed primarily of channels created within a rigid skeleton of disordered layers of carbon atoms, linked together by chemical bonds, stacked unevenly, creating a highly porous structure of nooks, crannies, cracks and crevices between the carbon layers. The activation of carbon is done by thermal decomposition in a furnace under a controlled atmosphere and heat. Activated carbon can be manufactured from coconut shell, peat, hard and soft wood, lignite coal, bituminous coal, olive pits and various carbonaceous specialty source. Activated carbon offers several advantages as a CO_2 adsorbent: an inherent affinity for CO_2 , an easy-to-design pore structure, insensitivity to moisture, ease of regeneration, stability over a large number of cycles, and an appealing low cost (Shafeeyan et al., 2015). Generally, the higher the internal surface area, the higher the effectiveness of the activated carbon. The surface area of activated carbon is impressive, range from $500 \text{ m}^2/\text{g}$ to $1500 \text{ m}^2/\text{g}$, or even more. A spoonful of the AC easily equates the surface area of a soccer field. Basically, the pore structure

of AC is classified into three major groups by International Union of Pure and Applied Chemistry (IUPAC) which were micropores (pore size < 2 nm), mesopores (pore size $2 - 50$ nm) and macropores (pore size > 50 nm). These pores provide large surface area for contaminants to be attached and hence make it favourable in industrial adsorption process. Physically, AC binds the material by Van der Waals force. Adsorption on AC can occur mainly due to the difference in adsorbate concentration in the solution, thus the adsorbate tends to migrate into the pore channels of AC.

2.7 Summary

Chapter two presents the adsorption process, theory of adsorption and also the adsorption isotherm. Next, it also reviewed different adsorbents' CO₂ adsorption performance. Besides, it also reviewed the effect of operating condition on the CO₂ adsorption. Moreover, this chapter also reviewed EAF steel slag and zeolites. Lastly, this chapter also reviewed the activated carbon and why activated carbon is chosen for adsorption.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

Granular coconut shell, Electric Arc Furnace steel slag, Sodium hydroxide (NaOH) (99%purity) was purchased from VWR Chemicals, and purified carbon dioxide (99.98%) and nitrogen (99.995%) as carrier gases were supplied by Wellgas Sdn. Bhd., Malaysia.

3.2 Equipment

In this study, the equipment used can be classified into the preparation of adsorbent, fixed-bed column adsorption system, analytical system and characterization of solid adsorbents.

3.2.1 Preparation of adsorbent

Memmert Universal Oven is used for the drying of the samples at 105 °C. Horizontal furnace is used for the activation of the sample at 800 °C (Figure 3-1). Teflon-lined autoclave (Figure 3-2) is used for the hydrothermal treatment of the samples.

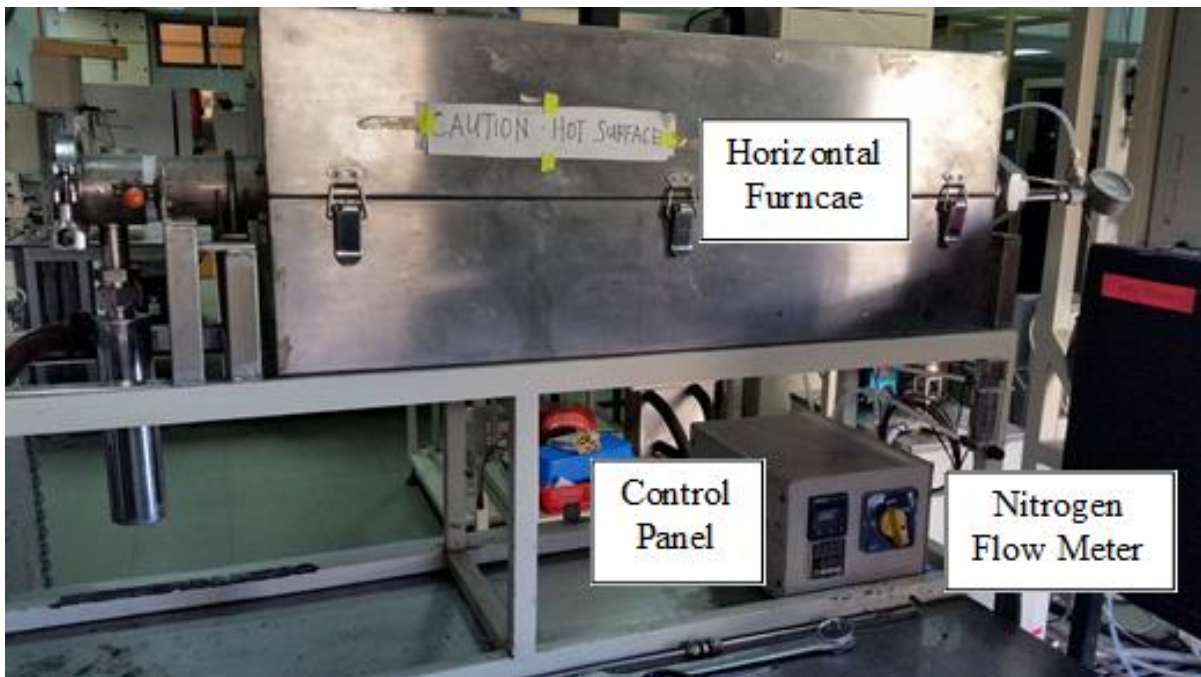


Figure 3-1 : Horizontal furnace used for activation of adsorbent.



Figure 3-2 : Teflon-lined autoclave in the oven for hydrothermal treatment.

3.2.2 Fixed-bed adsorption system

The schematic diagram of fixed-bed adsorption system is shown in the Figure 3-3 and the list of apparatus label is shown in Table 3.1. Besides, the experimental set-up for carbon dioxide adsorption is shown in Figure 3-4.

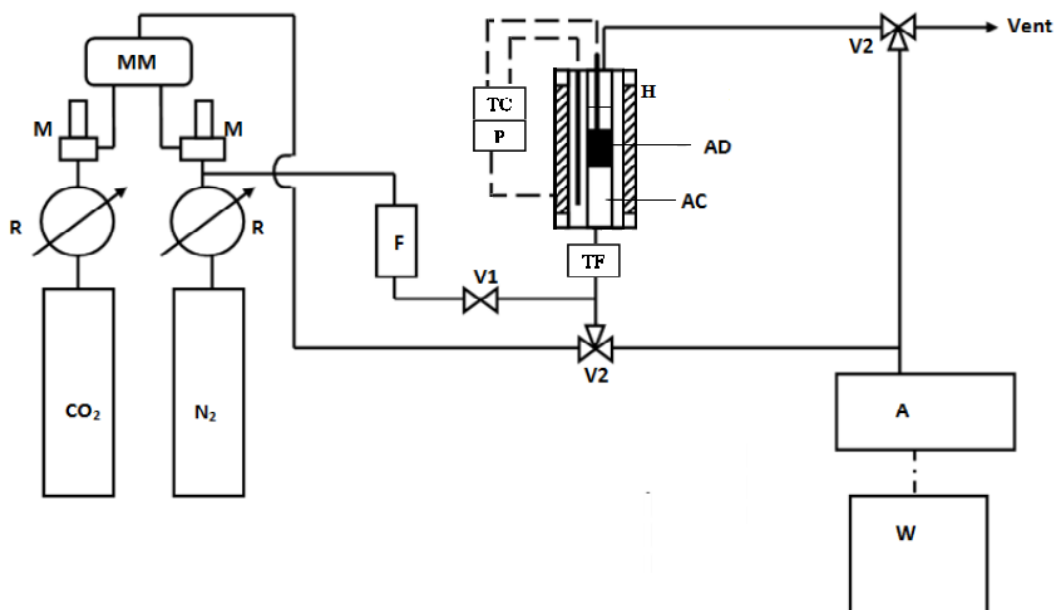


Figure 3-3 : The schematic diagram of fixed-bed column adsorption system.