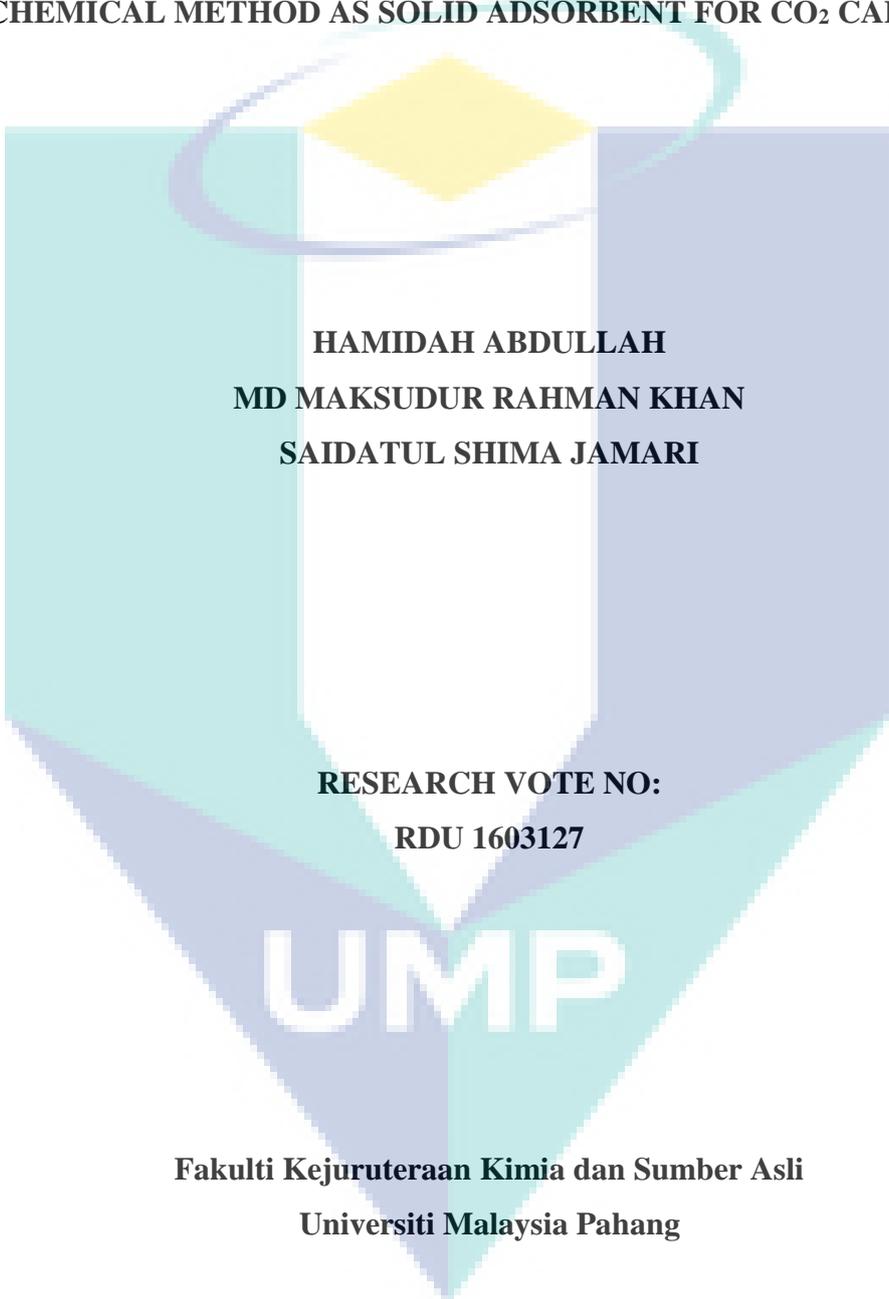


**MODIFICATION OF THE RICE HUSK ACTIVATED CARBON USING  
CHEMICAL METHOD AS SOLID ADSORBENT FOR CO<sub>2</sub> CAPTURE**

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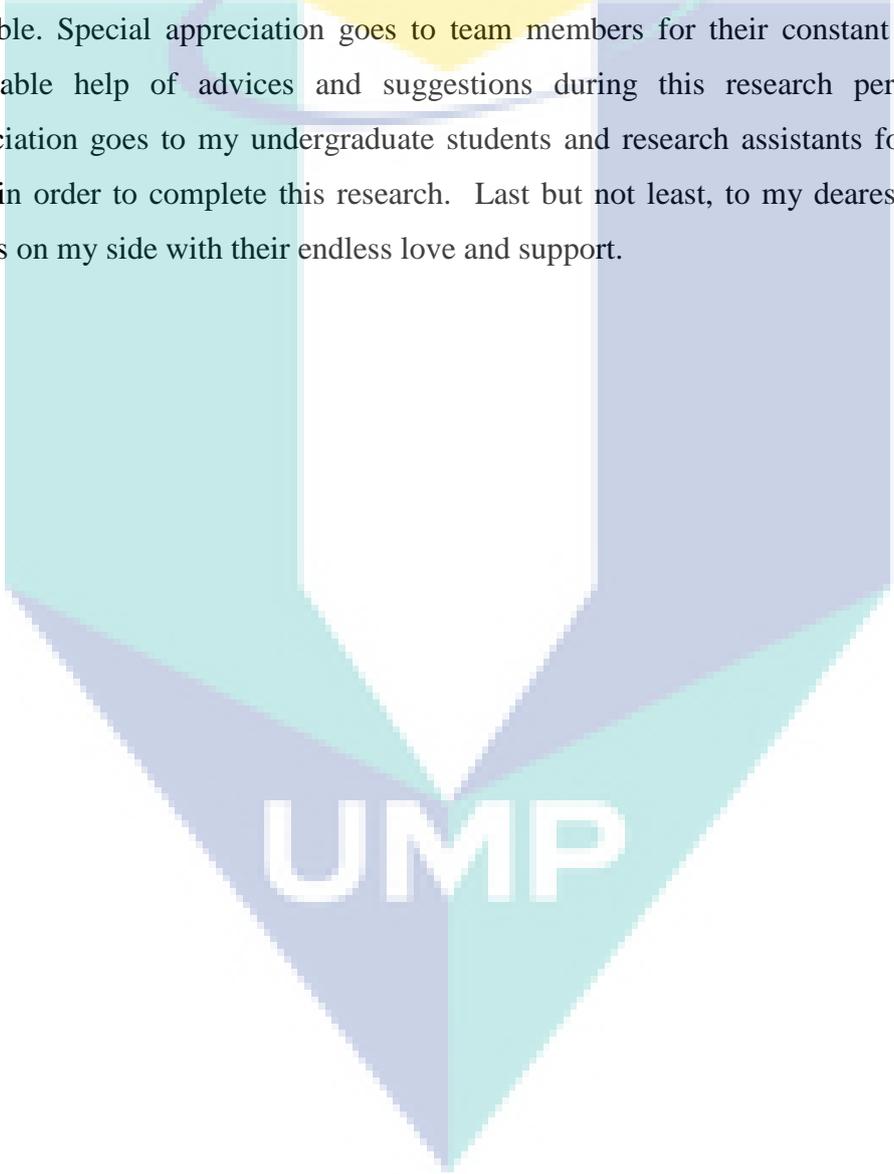
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**2019**

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## ABSTRACT

### MODIFICATION OF THE RICE HUSK ACTIVATED CARBON USING CHEMICAL METHOD AS SOLID ADSORBENT FOR CO<sub>2</sub> CAPTURE

*(Keywords: CO<sub>2</sub> capture, adsorption, activated carbon, chemically adsorb)*

Carbon dioxide (CO<sub>2</sub>) is one of the greenhouse gases that contributes to global warming. Therefore, it is crucial to develop technologies to overcome the increasing of CO<sub>2</sub> emission. One of the promising approach is CO<sub>2</sub> capture by adsorption process using solid adsorbent such as activated carbon (AC). The AC is attracted much attention due to its high surface area properties. The high surface area is required for physical interactions with CO<sub>2</sub> molecules. Besides, the chemical interactions between acidic CO<sub>2</sub> and the adsorbent could be occurring if the adsorbent has basic site.

Thus, this research has put a much effort to synthesis a new modified adsorbent that able to physically and chemically adsorb CO<sub>2</sub> to boost the CO<sub>2</sub> adsorption capacity. The commercial rice husk activate carbon has been used as adsorbent basis. Then, the chemically modification has been done by mixing the rice husk AC with polyethyleneimine (PEI), 3-triethoxysilylpropylamine (APTES) and ethylenediamine (EDA). The physicochemical properties of the synthesized adsorbents were then analyzed using Scanning Electron Microscopy (SEM), Fourier Transform Infra-red (FTIR) Spectroscopy, N<sub>2</sub> physisorption analysis and Thermogravimetric analysis (TGA). Besides, the performance of the synthesized adsorbents in CO<sub>2</sub> capture were also investigated.

In general, it was observed that the CO<sub>2</sub> adsorption capacity using modified-AC was enhanced compared to AC depending on the chemical used due to the change of physical and chemical properties. It can be concluded that the AC containing basic site have been successfully synthesized and the increase of CO<sub>2</sub> adsorption capacity using modified-AC was due to the additional basic site on the AC. The findings from this research are expected can contribute to the development of the existing CO<sub>2</sub> capture technology.

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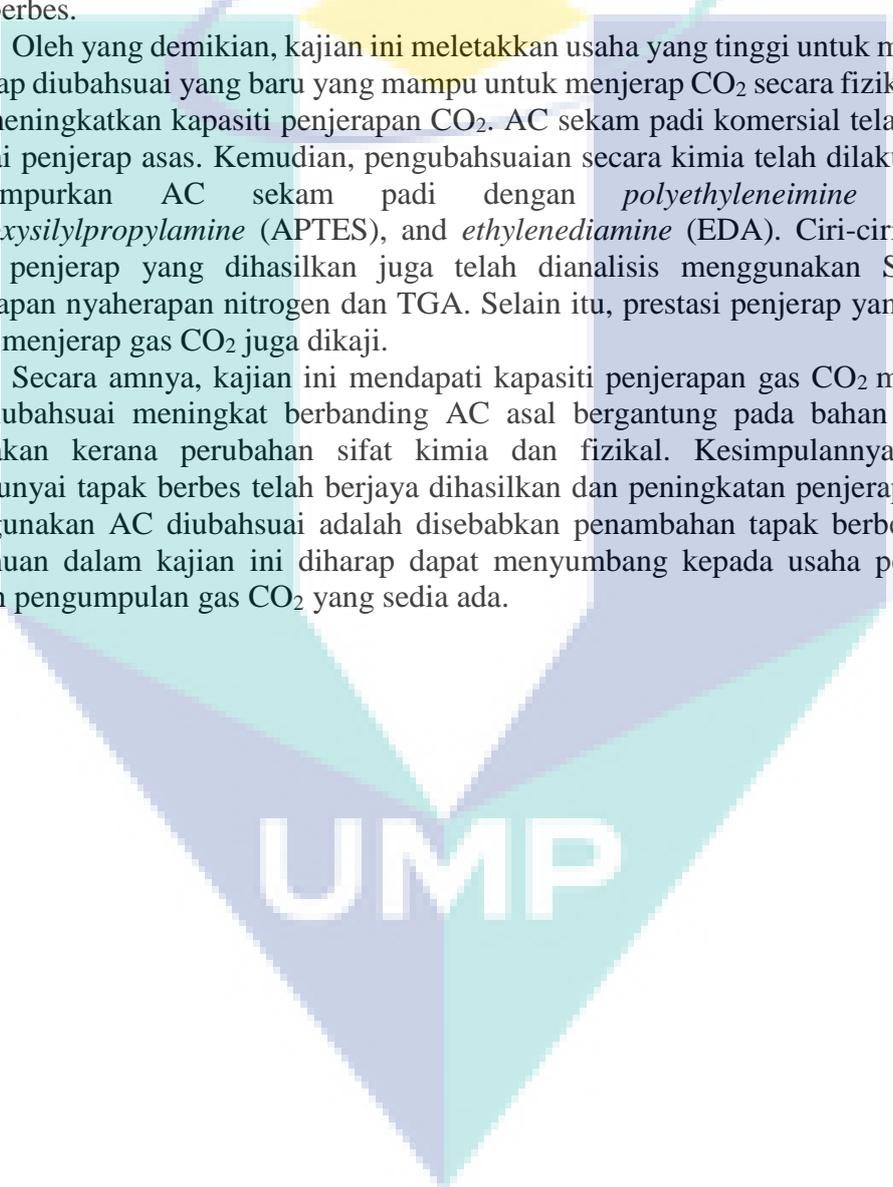
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## ABSTRAK

Karbon dioksida ( $\text{CO}_2$ ) merupakan salah satu gas rumah hijau yang menyumbang kepada pemanasan global. Oleh itu, pembangunan teknologi bagi mengatasi masalah peningkatan pembebasan gas karbon dioksida adalah amat diperlukan. Salah satu cara yang berkesan adalah dengan pengumpulan  $\text{CO}_2$  melalui kaedah penjerapan menggunakan penjerap pepejal seperti karbon diaktifkan (AC). AC mendapat perhatian kerana mempunyai sifat luas permukaan yang besar. Luas permukaan yang besar amat diperlukan untuk interaksi fizikal dengan molekul  $\text{CO}_2$ . Selain itu, interaksi kimia di antara  $\text{CO}_2$  yang berasid dan penjerap boleh berlaku sekiranya penjerap mempunyai tapak yang berbes.

Oleh yang demikian, kajian ini meletakkan usaha yang tinggi untuk menghasilkan penjerap diubahsuai yang baru yang mampu untuk menjerap  $\text{CO}_2$  secara fizikal dan kimia bagi meningkatkan kapasiti penjerapan  $\text{CO}_2$ . AC sekam padi komersial telah digunakan sebagai penjerap asas. Kemudian, pengubahsuaian secara kimia telah dilakukan dengan mencampurkan AC sekam padi dengan *polyethyleneimine* (PEI), *3-triethoxysilylpropylamine* (APTES), and *ethylenediamine* (EDA). Ciri-ciri fizikal dan kimia penjerap yang dihasilkan juga telah dianalisis menggunakan SEM, FTIR, penjerapan nyaherapan nitrogen dan TGA. Selain itu, prestasi penjerap yang dihasilkan dalam menjerap gas  $\text{CO}_2$  juga dikaji.

Secara amnya, kajian ini mendapati kapasiti penjerapan gas  $\text{CO}_2$  menggunakan AC diubahsuai meningkat berbanding AC asal bergantung pada bahan kimia yang digunakan kerana perubahan sifat kimia dan fizikal. Kesimpulannya, AC yang mempunyai tapak berbes telah berjaya dihasilkan dan peningkatan penjerapan gas  $\text{CO}_2$  menggunakan AC diubahsuai adalah disebabkan penambahan tapak berbes pada AC. Penemuan dalam kajian ini diharap dapat menyumbang kepada usaha pembangunan kaedah pengumpulan gas  $\text{CO}_2$  yang sedia ada.

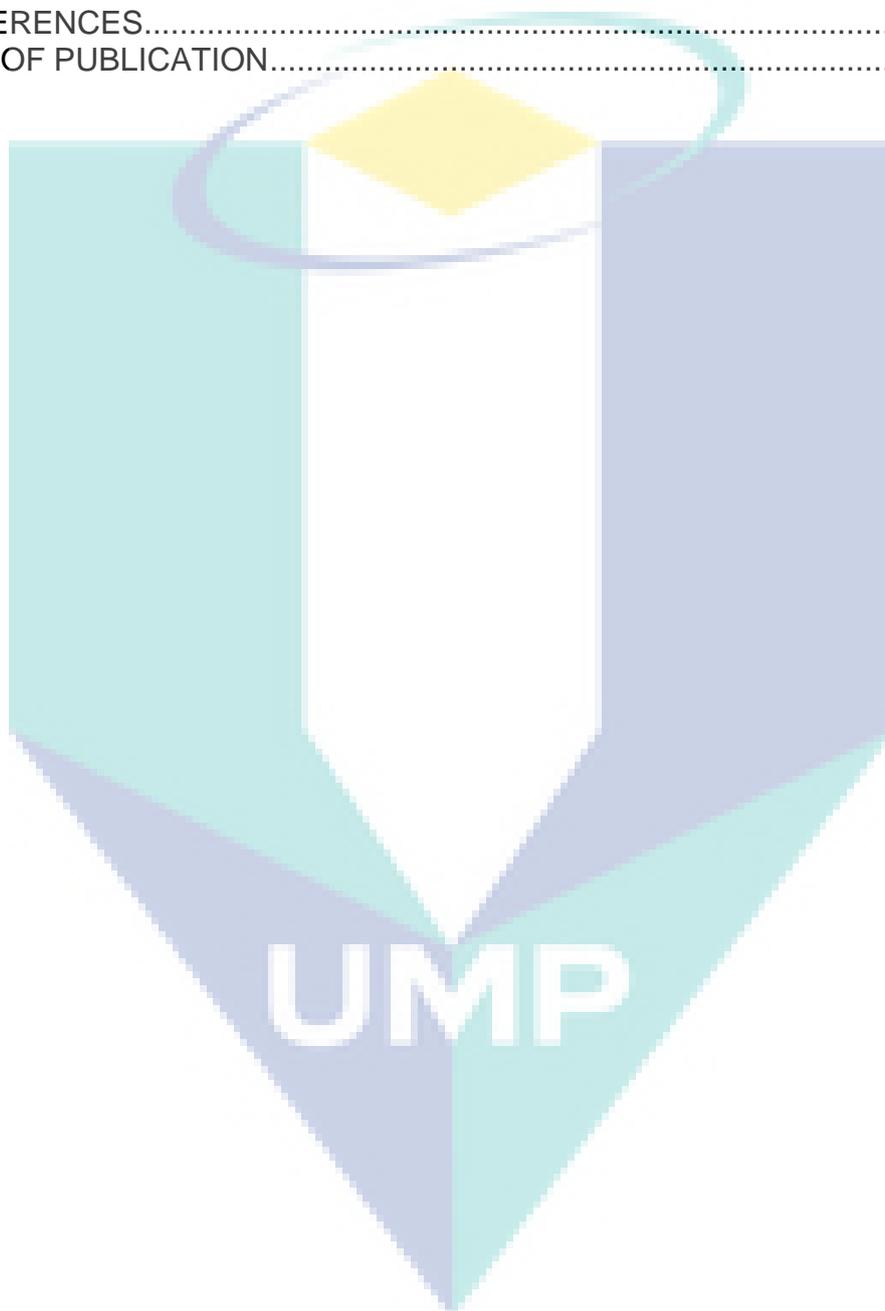


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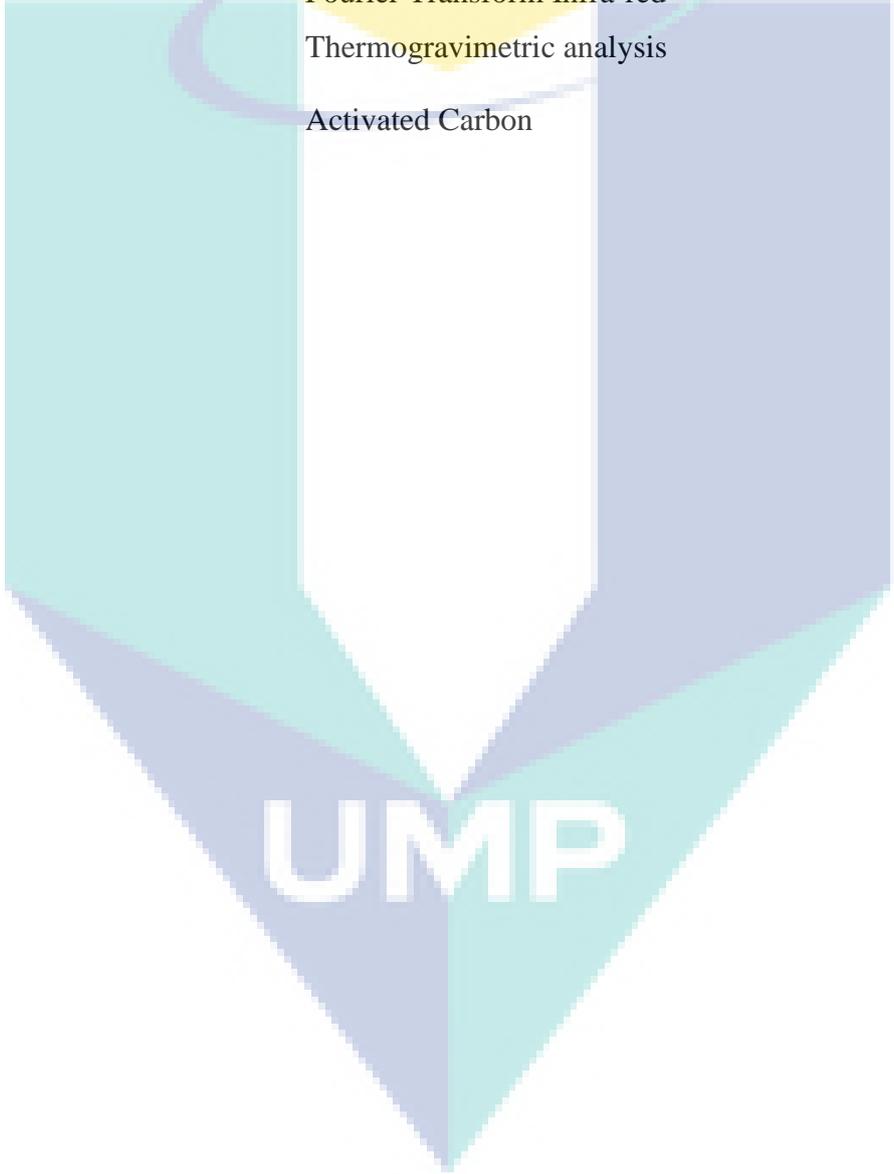
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## LIST OF ABBREVIATIONS

PEI	Polyethyleneimine
APTES	3-Triethoxysilylpropylamine
EDA	Ethylenediamine
CO <sub>2</sub>	Carbon dioxide
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infra-red
TGA	Thermogravimetric analysis
AC	Activated Carbon



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## CHAPTER 1

### INTRODUCTION

#### 1.1 Background of the study

Carbon dioxide (CO<sub>2</sub>) is the main greenhouse gas and anthropogenic CO<sub>2</sub> emissions are almost entirely caused by the fossil fuels used to produce energy. Rising of CO<sub>2</sub> emission is mainly caused by the utilization of non-renewable and carbon emitting fuels such as coal, petroleum and natural gas. Accelerated consumption of these resources undeniably causes lot of dreadful impacts towards the ecology, specifically the major long term climatic changes such as global warming (Rashidi, Yusup & Hon 2013). Global warming is largely contributed by CO<sub>2</sub>, followed by methane, ozone and chlorofluorocarbon. Floods, droughts, increased frequency of storms and a steady increase of global sea levels are the effect of global warming and environmental impacts (Hosseini et al. 2017). These greenhouse gases block the sun's energy from escaping to the space, and thus keep the atmosphere warm. Yet, rising level of greenhouse gases in the atmosphere causes the blanket to be thicker and accordingly, increases the surface temperature and eventually leads to global warming.

Various technologies can be used to separate carbon dioxide from effluent gas streams. The large-scale separation of CO<sub>2</sub> by absorption is a commercial operation used throughout the world. Other techniques, such as membrane separation and adsorption, focus on smaller-scale separations (Yang et al. 2008). Adsorption is considered one of the most appealing technologies that can be applied in industries due to the low energy requirement, cost advantage, and simplicity of applicability over a relatively wide range of temperatures and pressures (Heidari, Younesi, Rashidi, & Ghoreysi, 2014). Solid

adsorbent such as activated carbon was attracted most of the researcher to control or prevent this problem due to its properties such as have a high surface area. Activated carbon is the common adsorbent used in adsorption industries whereby it provides a large spectrum of pore structures and surface chemistry for gas adsorption. An easy to use, regenerate, multi-cycle and high adsorption capacity adsorbent is the yening for global community in curbing carbon dioxide environmental pollution (Auta & Hameed, 2014). Generally, activated carbons are relatively cheap, stable in acidic or basic solutions and cost effective as well as can be regenerated after used (Yin, Aroua & Daud 2008).

The adsorbent that was chosen in this study is a carbon-based adsorbent. Carbon-based adsorbent has high adsorption capacity for CO<sub>2</sub> (Yong, Mata & Rodrigues 2001). Activated carbons is attractive as CO<sub>2</sub> adsorbent due to its wide availability, high thermal stability, low cost, and low sensitivity to moisture (Rashidi, Yusup, & Hon, 2013). There are several methods by which activated carbons can be modified to improve their adsorption capacity, including oxidation, heat treatment, chemical treatment with acidic, basic solutions or metallic species, etc. The best method to enhance the CO<sub>2</sub> adsorption capacity is by promoting basic species such as alkanolamine on the surface of activated carbon through chemical impregnation (Lee et al. 2013). The surface basicity of the activated carbon lead to a higher amount of nitrogen-bearing surface groups which result in higher CO<sub>2</sub> adsorption capacity.

Considering cost effectiveness in activated carbon production, researchers developed different precursors from abundant waste materials, such as palm shells, sea mango, cocoa pod shells, and rice husk (Zulkurnai et al. 2017). Activated carbon from rice husk is one of the biomass activated carbon come from waste source that have a big potential to be used as CO<sub>2</sub> adsorbent. The presence of hydrocarbon such as cellulose and lignin made the rice husk suitable for preparation of activated carbons. Porous carbon derived from the rice husks has wide availability, fast kinetics and appreciable adsorption capacities. Rice husk that carries a hydrocarbon chain contains many pores with high surface area which perfectly meets the characteristics of a good adsorbent (Masoum Raman et al. 2016).

## 1.2 Motivation

Development of modern civilization has led to rapid utilization of fossil fuels. As a consequence, emission of CO<sub>2</sub> has substantially increased. CO<sub>2</sub> is released to atmosphere as a component in flue gases emitted by power plants, gas processing industries, refineries, chemical and petrochemical industries, iron and steel industries and cement industries. These industries are mainly responsible for anthropogenic CO<sub>2</sub> emissions. The International Panel on Climate Change (IPCC) estimates that average CO<sub>2</sub> concentration level may rise to 570 ppm by the year 2100 causing an increase in mean sea level height in the reference is 38 cm and the rise in mean global average temperature of about 1.9 °C (Singh, & Anil Kumar 2016). Several approaches have been suggested and implemented for reducing the concentration level of CO<sub>2</sub> in the environment and the best approach is capturing CO<sub>2</sub> from power industries.

Beside domestic consumption, rice is a major agricultural product that extremely high exportation value. In rice manufacturing, rice husk is the by-product from paddy grinding. Rice husk is the outermost layer of paddy grain which is produced in the first step of milling process and makes up about 20% of the rice (paddy) (Cheenmatchaya, & Kungwankunakorn 2014). In majority of rice producing countries much of the husk produced from processing of rice is either burnt or dumped as waste. Burning of rice husk in ambient atmosphere leaves a residue, called rice husk ash which will cause damage to land and surrounding area where it is dumped (Mohanta, K. Kumar, D. & Prakash 2012). The estimated annual rice production is very high, so this will contribute high production of rice husk hence these waste products must be utilized (Korobochkin, Tu & Hieu 2016).

In order to reduce the concentration of CO<sub>2</sub> in the atmosphere and the production of waste from rice husk, study of CO<sub>2</sub> adsorption using rice husk activated carbon is investigated to optimize the use of rice husk and reduce the concentration CO<sub>2</sub> in atmosphere. There was reported that the rice husk can be processed with activated carbon. Therefore, CO<sub>2</sub> adsorption using rice husk activated carbon give the best solution to solve both problems which are CO<sub>2</sub> emission and rice husk waste.

### 1.3 Problem Statement

Activated carbon have been found to present some challenges such as low adsorption capacity at high temperatures and poor selectivity to carbon dioxide (Yadavalli et al. 2017). Adsorption from activated carbon rice husk is mostly physically adsorbed. These can be overcome by chemically and physically modifying the activated carbon surface to capture the target compound. The carbon-based materials sorption capacity can be improved by using amine solution as the impregnator of the porous materials as the amine is characterized by a high absorption capacity in relation to CO<sub>2</sub> (Masoum Raman et al. 2016). CO<sub>2</sub> is a weak Lewis acid, therefore introduction of basic nitrogen containing functional groups enables the surface to interact strongly with CO<sub>2</sub> thus enhancing the adsorption capacity of the activated carbon (Yadavalli et al., 2017). Comprehensive study on the effect of impregnation of polyethyleneimine (PEI), 3-triethoxysilylpropylamine (APTES), potassium hydroxide (KOH) and ethylenediamine (EDA) on the surface physicochemical characteristics of activated carbon from rice husk had not been done before and this chemical will be expected to improve the existing amine modified activated carbon performance.

### 1.4 Objectives

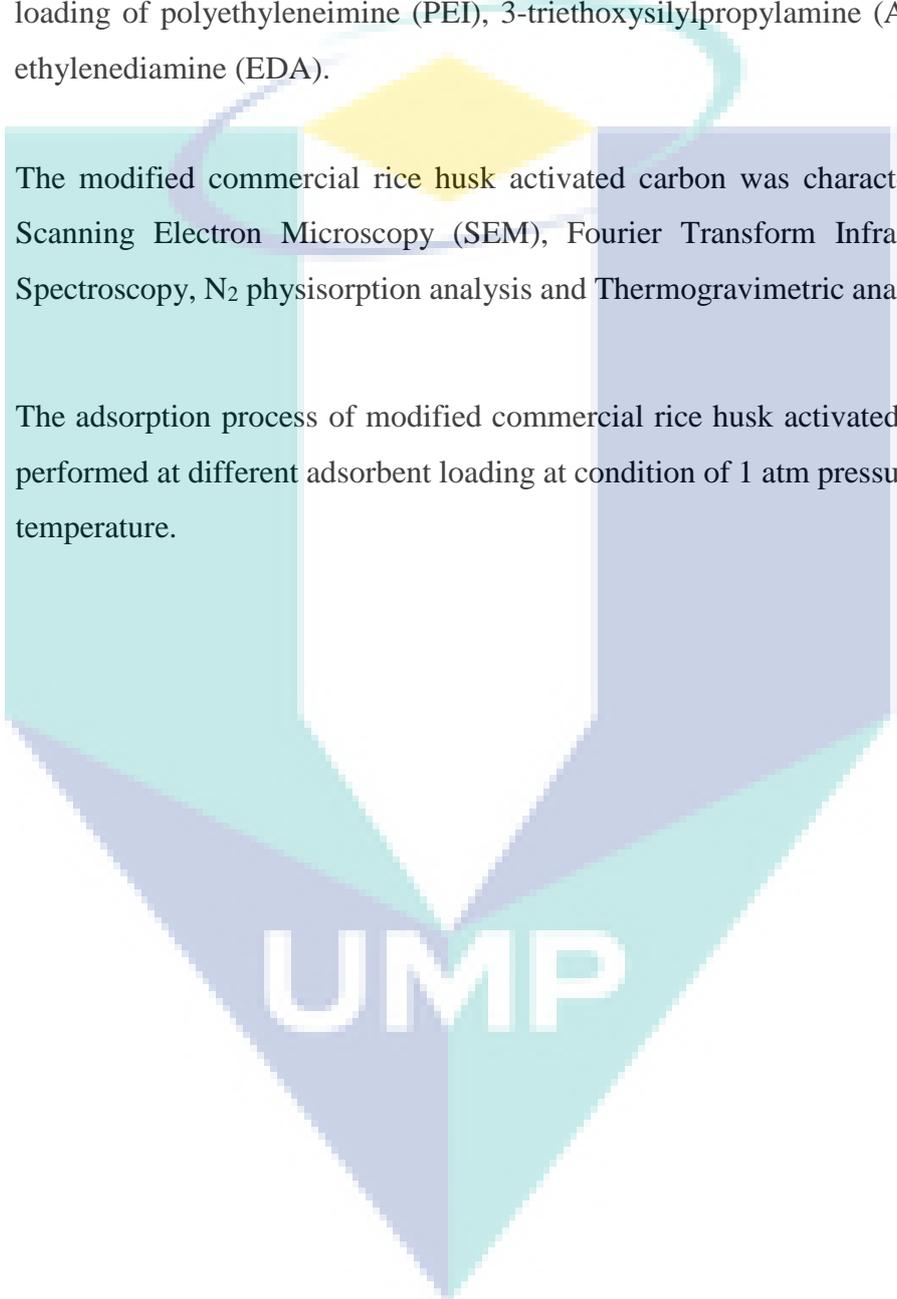
The following are the objectives of this research:

- 1) To synthesis and characterize the chemically modified commercial rice husk activated carbon using polyethyleneimine (PEI), 3-triethoxysilylpropylamine (APTES), and ethylenediamine (EDA).
- 2) To investigate the performance of modified activated carbon in CO<sub>2</sub> adsorption using continuous packed bed adsorption column.

## 1.5 Scopes of Study

The following are the scope of this research:

- 1) The chemically modified commercial rice husk activated carbon was synthesized by impregnating the commercialized rice husk activated carbon with different loading of polyethyleneimine (PEI), 3-triethoxysilylpropylamine (APTES), and ethylenediamine (EDA).
- 2) The modified commercial rice husk activated carbon was characterized using Scanning Electron Microscopy (SEM), Fourier Transform Infra-red (FTIR) Spectroscopy, N<sub>2</sub> physisorption analysis and Thermogravimetric analysis (TGA).
- 3) The adsorption process of modified commercial rice husk activated carbon was performed at different adsorbent loading at condition of 1 atm pressure, and 25°C temperature.



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## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 CO<sub>2</sub> Capture Technology

Capture of CO<sub>2</sub> contributes 75 percent to the overall carbon capture and storage (CCS) cost and CCS increases the electricity production cost by 50 percent (Yang et al. 2008). Although these numbers may vary with different CCS schemes, cutting the capture cost is the most important issue for the CCS process to be acceptable to the energy industry. There are many options for CO<sub>2</sub> separation and capture, and these include adsorption, absorption, membrane and biotechnology. Carbon dioxide capture using solid adsorbents is considered as one of the most promising technologies for carbon capture and storage (CCS). Gas adsorption is a separation process in which a gaseous component is separated from a gas stream by the use of a solid material (Spigarelli, & Kawatra 2013). Table 2.1 shows the advantage and disadvantage of different technologies used in CO<sub>2</sub> separation and capture.

**Table 2.1:** Comparison of different separation technologies (Leung, Caramanna & Maroto-Valer 2014)

Technology	Advantages	Disadvantages
Absorption	<ul style="list-style-type: none"><li>• High absorption efficiency (&gt; 90%)</li><li>• Sorbents can be regenerated by heating and/or depressurization</li><li>• Most mature process for CO<sub>2</sub> separation</li></ul>	<ul style="list-style-type: none"><li>• Absorption efficiency depends on CO<sub>2</sub> concentration</li><li>• Significant amounts of heat for absorbent regeneration are required</li><li>• Environmental impacts related to sorbent degradation have to be understood</li></ul>

Adsorption	<ul style="list-style-type: none"> <li>• Process is reversible and the adsorbent can be recycled</li> <li>• High adsorption efficiency achievable (&gt; 85%)</li> </ul>	<ul style="list-style-type: none"> <li>• Require high temperature adsorbent</li> <li>• High energy required for CO<sub>2</sub> desorption</li> </ul>
Membrane separation	<ul style="list-style-type: none"> <li>• Process has been adopted for separation of other gases</li> <li>• High separation efficiency achievable (&gt; 80%)</li> </ul>	<ul style="list-style-type: none"> <li>• Operational problems include low fluxes and fouling</li> </ul>
Cryogenic separation	<ul style="list-style-type: none"> <li>• Mature technology</li> <li>• Adopted for many years in industry for CO<sub>2</sub> recovery</li> </ul>	<ul style="list-style-type: none"> <li>• Only viable for very high CO<sub>2</sub> concentration (&gt;90% v/v)</li> <li>• Should be conducted at very low temperature</li> <li>• Process is very energy intensive</li> </ul>

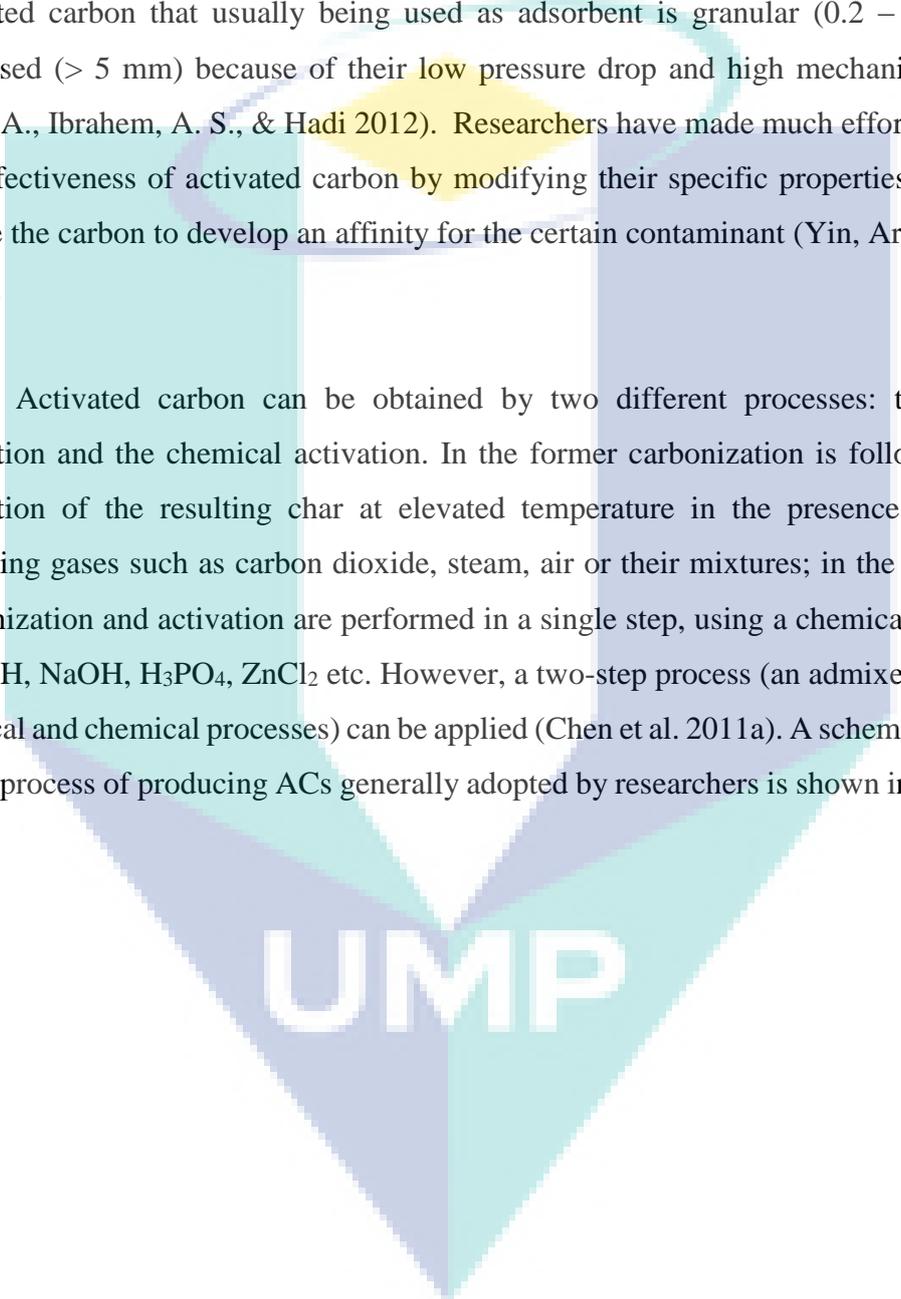
Currently, absorption using amine solutions is the technology that is more studied and it is commercially used for CO<sub>2</sub> capture in power plants. The major drawback in using amine solutions are high energy consumption, degradation and vaporization of solvent and corrosion of process equipment (Shafeeyan et al. 2010). Adsorption is considered to be a promising method, because of its low energy consumption, low cost, high stability over wide range of pressure and temperature (LI et al. 2010) and the sorbent could be dispose safely after use. Adsorbents such as silica, metal oxides, metal organic frame works, zeolites and AC have been tested for CO<sub>2</sub> capture. Carbon based materials are considered to be promising CO<sub>2</sub> capture adsorbents due to their low cost, high surface area, high amenability to surface functionalization and pore structure modifications (Wang et al. 2013). Currentlly, researches showed that carbon based materials are capable of removing CO<sub>2</sub> together with other gaseous pollutants individually and simultaneously.

## 2.2 Activated Carbon as Adsorbent

Activated carbon is made from carbonaceous material of any types of substances such as wood, lignite, anthracite or bone. It is considered as highly potential adsorbent for gas adsorption. Activated carbon has been established as effective adsorbents for the removal of a wide variety of pollutants dissolved in aqueous media, or from gaseous environment due to its exceptionally large surface areas, high adsorption capacity, high purity standard, well-developed internal microporosity structure as well as the presence of a wide spectrum of surface functional groups (Li et al. 2009; Yin et al. 2008). Activated carbon was selected for its low cost of raw materials and for the good yield obtained

because of well-developed porosity (Li et al. 2009). Activated carbons are inexpensive and insensitive to moisture. They exhibit high surface area, high CO<sub>2</sub> adsorption capacity and thermal stability (Singh, & Anil Kumar 2016). Large surface area is a result of creation of additional micropores and probably widening of the existing one, hence, increase in active sites as well as accessibility to the sites (Uçar et al. 2009). The types of activated carbon that usually being used as adsorbent is granular (0.2 – 5 mm) and palletised (> 5 mm) because of their low pressure drop and high mechanical strength (Dali, A., Ibrahim, A. S., & Hadi 2012). Researchers have made much effort to increase the effectiveness of activated carbon by modifying their specific properties in order to enable the carbon to develop an affinity for the certain contaminant (Yin, Aroua & Daud 2007).

Activated carbon can be obtained by two different processes: the physical activation and the chemical activation. In the former carbonization is followed by the activation of the resulting char at elevated temperature in the presence of suitable oxidizing gases such as carbon dioxide, steam, air or their mixtures; in the second one, carbonization and activation are performed in a single step, using a chemical agent such as KOH, NaOH, H<sub>3</sub>PO<sub>4</sub>, ZnCl<sub>2</sub> etc. However, a two-step process (an admixed method of physical and chemical processes) can be applied (Chen et al. 2011a). A schematic diagram of the process of producing ACs generally adopted by researchers is shown in Figure 2.1.



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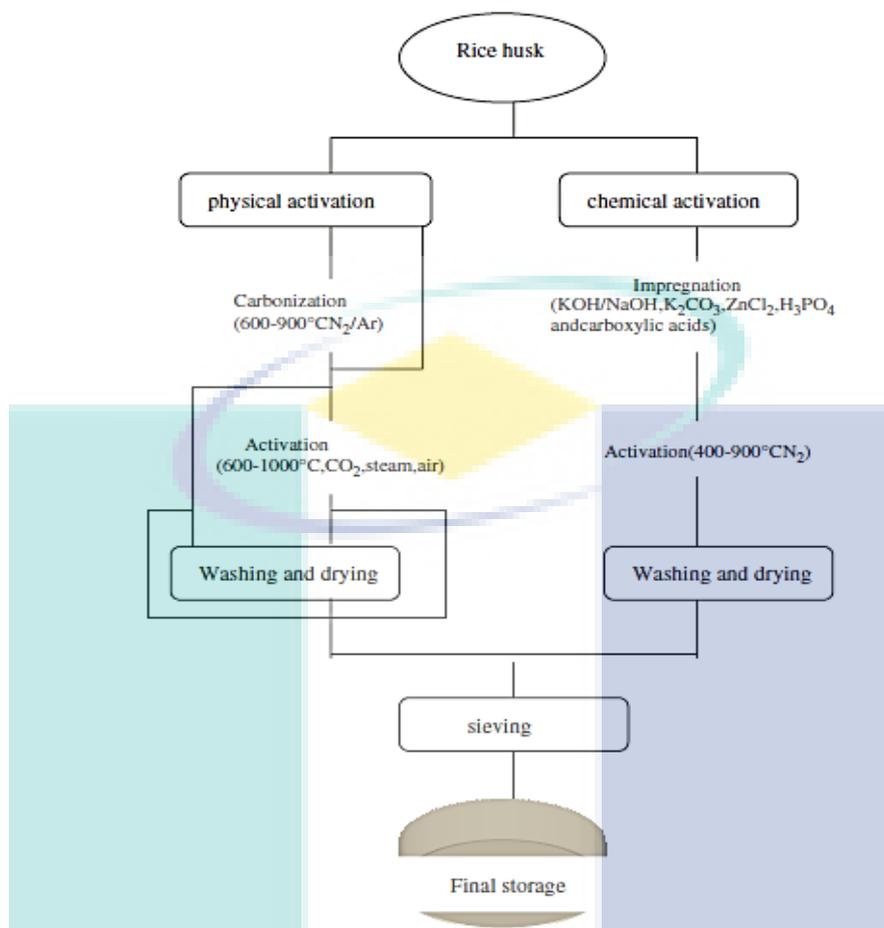


Figure 2. 1: Principle scheme of the ACs preparation from rice husk

### 2.2.1 Chemically Modified Activated Carbon

AC have been found to present some challenges such as low adsorption capacity at high temperatures and poor selectivity to carbon dioxide, these can be overcome by chemically modifying the AC surface to capture the target compound (Yadavalli et al. 2017). The physical and surface chemical properties of ACs can be modified by several different oxidation procedures, heat treatments and/or impregnation procedures; during those treatments, the types and amounts of oxygen and nitrogen-bearing surface groups, which play an important role in the adsorption behaviours of the ACs, are changed (Caglayan, & Aksoylu 2013). Recently, several excellent research initiatives have been taken to removal of CO<sub>2</sub> by modified AC as an adsorbent. Since the CO<sub>2</sub> molecule are categorized as a Lewis acid, affinity of AC towards CO<sub>2</sub> gas can be carried out according to the chemical treatment, by increasing their basicity properties through neutralization of acidic functional group, or to replace acidic group to basic functionalities. Table 2.2 shows the types of carbon already been used for CO<sub>2</sub> adsorption with their modification.

**Table 2.2:** Types of carbon with surface modification and their performance in CO<sub>2</sub> capture

Type Of Adsorbent	Percentage of CO <sub>2</sub> Adsorption Capacity	Remarks	References
Impregnation of palm shell-based AC with sterically hindered amines	The CO <sub>2</sub> adsorption capacity increased to 64.0 mgCO <sub>2</sub> /gsorbent (AMP-AC), 54.0 mgCO <sub>2</sub> /gsorbent (AMPD-AC) and 44.3 mgCO <sub>2</sub> /gsorbent (MMEA-AC) respectively	Use of sterically hindered amines which have a bulky substituent adjacent to the amino group can lower the stability of the carbamate and allow the CO <sub>2</sub> adsorption to be more effective	(Lee et al. 2013)
Impregnation of granular coconut shell AC with NaOH	The unmodified AC (without NaOH loading) can adsorb 17.52 mg/g CO <sub>2</sub> , whereas the 24%, 32%, 40% and 48% NaOH modified adsorbents can adsorb 24.10, 27.10, 21.69, and 23.24 mg/g CO <sub>2</sub> , respectively.	Treatment with an alkaline compound can provide more active functional sites for CO <sub>2</sub> . Activation with sodium hydroxide (NaOH) is more effective in the preparation of activated porous carbon	(Tan. Y.L et al. 2014)
Impregnation of ammonia solution on eucalyptus wood based activated carbon	The maximum adsorption capacities estimated for AC-unmodified, AC-NH-400 and AC-NH-800 were 28.01 mmol/g, 6.93 mmol/g, and 31.61 mmol/g at 303 K, respectively.	Introduction of nitrogen functional groups into the carbon surface can increase the adsorption capacity of AC for CO <sub>2</sub> adsorption	(Heidari et al. 2014)
Impregnation of AC with two metal oxides Cr <sub>2</sub> O and Fe <sub>2</sub> O <sub>3</sub>	Impregnation of Cr <sub>2</sub> O increased the CO <sub>2</sub> adsorbed by about 20% in compared to unmodified AC, while Fe <sub>2</sub> O <sub>3</sub> was not an effective impregnating species. Co-impregnation of Cr <sub>2</sub> O with zinc carbonate hydroxide led to another 5% increase in CO <sub>2</sub> capture capacity.	Introduction of metallic species as surface additives can modify the adsorptive properties of ACs. Two surface treatments as conventional solution and slurry	(Hamza, Shawal & Nasri 2015)

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impregnation  
methods were used  
to modify surface  
properties of the AC

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In comparison to physical activation, chemical activation provides two important advantages. One is the lower temperature at which the process is performed. The other is that the global yield of chemical activation tends to be greater because burn off char is not required. Besides, part of the added chemicals (such as zinc salts and phosphoric acid), can be easily recovered (Chen et al. 2011a)

Moreover, chemical activation has been shown as an efficient method to obtain carbons with high surface area and narrow micropores distribution (Adinata, Wandaud & Aroua 2007) The surface chemistry of the ACs can be efficiently modified by chemical impregnation which together with the intrinsic nature of the AC can highly increase the adsorption capacity (Somy et al. 2009). With these studies in mind, it is therefore suggested that long-chained polymer which consists predominantly of hydrocarbon components with attached amine groups will be an ideal impregnation compound for enhancing CO<sub>2</sub> affinity of AC at the same time, enhances its selectivity.

### **2.2.2 Rice Husk as Activated Carbon**

Paddy rice (*Oryza sativa*) is a staple food of over half the world's population and about one-fifth of the world's population is engaged in rice cultivation. The global paddy rice production continued to increase at an average rate of 16.48 million tonnes per year during the last ten years, reaching about 718.3 million tonnes in 2011 with an estimated value of US\$ 240 billion (Zhang et al. 2014).

Rice husk, an unwanted agriculture mass scum and protecting covering grain rice which is a by-product of the rice milling industry. It is one of the most important agricultural residues in quantity. 78% of weight as rice, broken rice and bran, rest 22% of weight of paddy as husk (Ghosh 2013). Rice husk has been successfully used as fuel in

many industrial factories and used as biomass fuel in electricity generating because of its low humidity and simple operation (Cheenmatchaya, & Kungwankunakorn 2014).

Rice husks are usually used as a low-value energy resource, burned in the field, or discarded, which are unfavorable to environment. The processing and transformation of rice husks into AC with good adsorption properties would alleviate problems of disposal and management of these waste by-products, while producing value added products from rice husks for water and wastewater treatment etc., to expand the carbon market (Chen et al. 2011a).

However, the amounts of rice husk available are so far in excess of any local uses and have posed disposal problems. The main purpose for choosing rice husk as adsorption agent is due to its granular structure, chemical stability and its local availability at very low cost (Masoud et al. 2016). The rice husk compositions are: 32.24% cellulose, 21.34% hemicellulose, 21.44% lignin, 1.82% extractives, 8.11% water and 15.05% mineral ash. The mineral ash is 94.5–96.34% SiO<sub>2</sub> (Daifullah, Girgis & Gad 2004). The presence of large amount of hydrocarbon such as cellulose and lignin content made the rice husk to be used as a raw material for preparation of activated carbons that contain complex porous structures (Mohanta, K. Kumar, D. & Prakash 2012). The rice husk has been processed as activated carbon can be used widely in many applications such as chemical adsorbent and fuel in power plant. The high availability and low price makes extra benefit towards the use of this material in many industries.

### **2.2.3 Impregnation of Amine with Rice Husk Activated Carbon**

While activated carbon have been found to present some challenges such as low adsorption capacity at high temperatures and poor selectivity to carbon dioxide, these can be overcome by chemically modifying the activated carbon surface to capture the target compound (Yadavalli et al. 2017). Carbon-based materials are abundant, cheap, easy to make, and chemically and hydrothermally stable, but their selectivity for CO<sub>2</sub> and other acidic gases is low in the presence of other gases such as N<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub> (Rashidi et al. 2013). The presence of hydrocarbon such as cellulose and lignin made the rice husk suitable for preparation of activated carbons (Singh, & Anil Kumar 2016). Porous carbon derived from the rice husks has wide availability, fast kinetics and appreciable adsorption

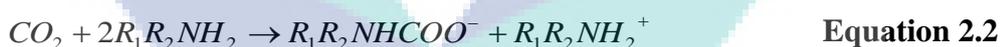
capacities (Chen et al. 2011a). Rice husk that carries a hydrocarbon chain contains many pores with high surface area which perfectly meets the characteristics of a good adsorbent.

Amine-modified adsorbents actually make use of the amine groups grafted or loaded on the porous materials to adsorb CO<sub>2</sub> as the amine is characterized by a high absorption capacity in relation to CO<sub>2</sub> (Chen et al. 2011a). CO<sub>2</sub> adsorption capacity also can be enhanced by impregnation of amine and ammonia on the surface of adsorbent (Boonpoke et al. 2011). The carbon based material is high in alkalinity and the amine will be stabilized on the surface so that the amine can be prevented from dissociating. In the direct method, amine will condense with carboxyl group on the activated carbon to form amide which is used in CO<sub>2</sub> captured (Shafeeyan et al. 2010). The impregnation of large amounts of amines is good on the mesoporous carbons having high surface area, large pore volumes and specific surface properties. Alkanolamine such as primary amine and secondary amine will react with CO<sub>2</sub> which involves the mass transfer of CO<sub>2</sub> from the gas phase into the aqueous phase of amine in a series of the reactions as Equation 2.1 and 2.2 (Masoum Raman et al. 2016):

Primary amine



Secondary amine



Potential to be CO<sub>2</sub> adsorbent after the surface modification has been made on the rice husk activated carbon with alkanolamine solution. The presence of amine on the surface of the adsorbent is expected to enhance the CO<sub>2</sub> adsorption capacity (Boonpoke et al. 2011).

#### 2.2.4 Basicity of Activated Carbon

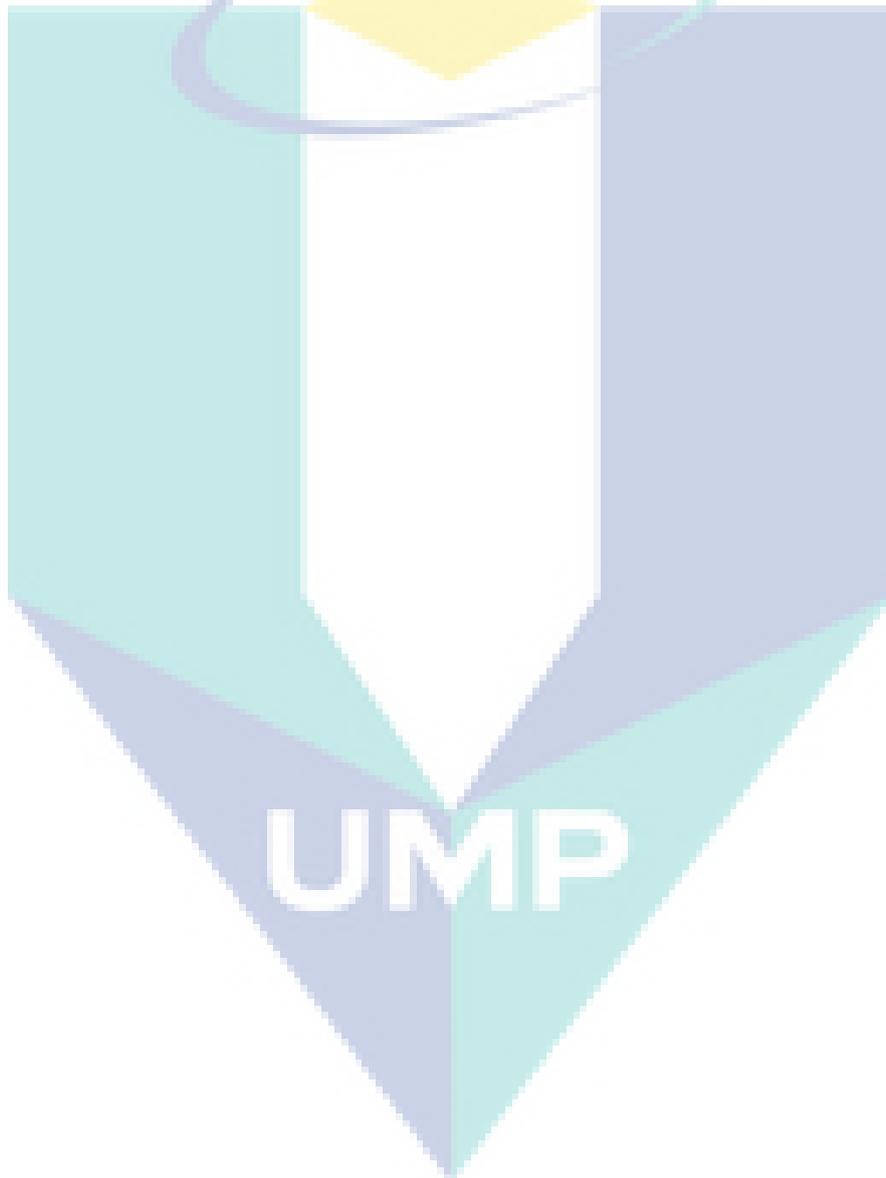
One of the popular ways used for the preparation of activated carbon with increased basicity is to remove or neutralize the acidic functionalities, and other way is to replace acidic groups with proper basic groups (e.g., basic nitrogen functionalities). It has

been shown that introduction of nitrogen functional groups into the carbon surface can increase the capacity of activated carbon to adsorb CO<sub>2</sub>. Nitrogen containing functionalities can be introduced through either reaction with nitrogen containing reagents (such as NH<sub>3</sub>, nitric acid, and amines) or activation with nitrogen containing precursors. The objective of ammonia treatment is to increase the basicity of activated carbon by introducing basic nitrogen functionalities to the carbon surface. When the carbon materials are treated with ammonia at high temperatures, ammonia will decompose to free radicals such as NH<sub>2</sub>, NH, and atomic hydrogen and nitrogen. Those free radicals attack the carbon to form nitrogen containing functional groups. Several authors have studied thermal treatment of carbons in an ammonia atmosphere. Economy et al. treated activated carbon fibers (ACF) using NH<sub>3</sub> at elevated temperature to obtain a product with basic characteristics. Some researchers proposed the modification of activated carbon with gaseous ammonia as a suitable technique to produce efficient CO<sub>2</sub> adsorbents. Various characterization methods have been used to detect and verify the existence of surface functional groups of the activated carbons. The most common of these methods are chemical titration, temperature programmed desorption (TPD), X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FT-IR).

Basicity of activated carbon can be associated with resonating pi-electrons ( $\pi$ ) of carbon aromatic rings that attract protons, and basic surface functionalities (e.g., nitrogen containing groups) that are capable of binding with protons. It was proposed that certain oxygen containing surface functionalities such as chromene, ketone, and pyrone can contribute to the carbon basicity. However, the basic character of activated carbons arises primarily from delocalized  $\pi$ -electrons of graphene layers. It was pointed out that the  $\pi$ -electrons of these layers could act as Lewis bases. Some researchers studied the contribution of basal planes to the carbon basicity. The surface basicity of two series carbons and demonstrated that oxygen-free carbon sites can adsorb protons from solution. These sites are located in  $\pi$ -electron rich regions on the basal plane of carbon crystallites. Therefore, basic sites are Lewis type associated with the carbon structure itself (Shafeeyan et al. 2010).

It has been shown that introduction of nitrogen functional groups into the carbon surface can increase the capacity of activated carbon to adsorb CO<sub>2</sub>. Nitrogen containing

functionalities can be introduced through either reaction with nitrogen containing reagents (such as  $\text{NH}_3$ , nitric acid, and amines) or activation with nitrogen containing precursors. Possible structures of the nitrogen functionalities include the following: amide group, imide group, lactame group, pyrrolic group, and pyridinic group. Nitrogen functionalities generally provide basic property, which can enhance the interaction between carbon surface and acid molecules such as, dipole–dipole, H-bonding, covalent bonding, and so on (Shafeeyan et al. 2010).



## CHAPTER 3

### METHODOLOGY

#### 3.1 Introduction

This chapter describes the list of materials and methodology used in this research.

Figure 3.1 shows the flow diagram of the methodology in this research.

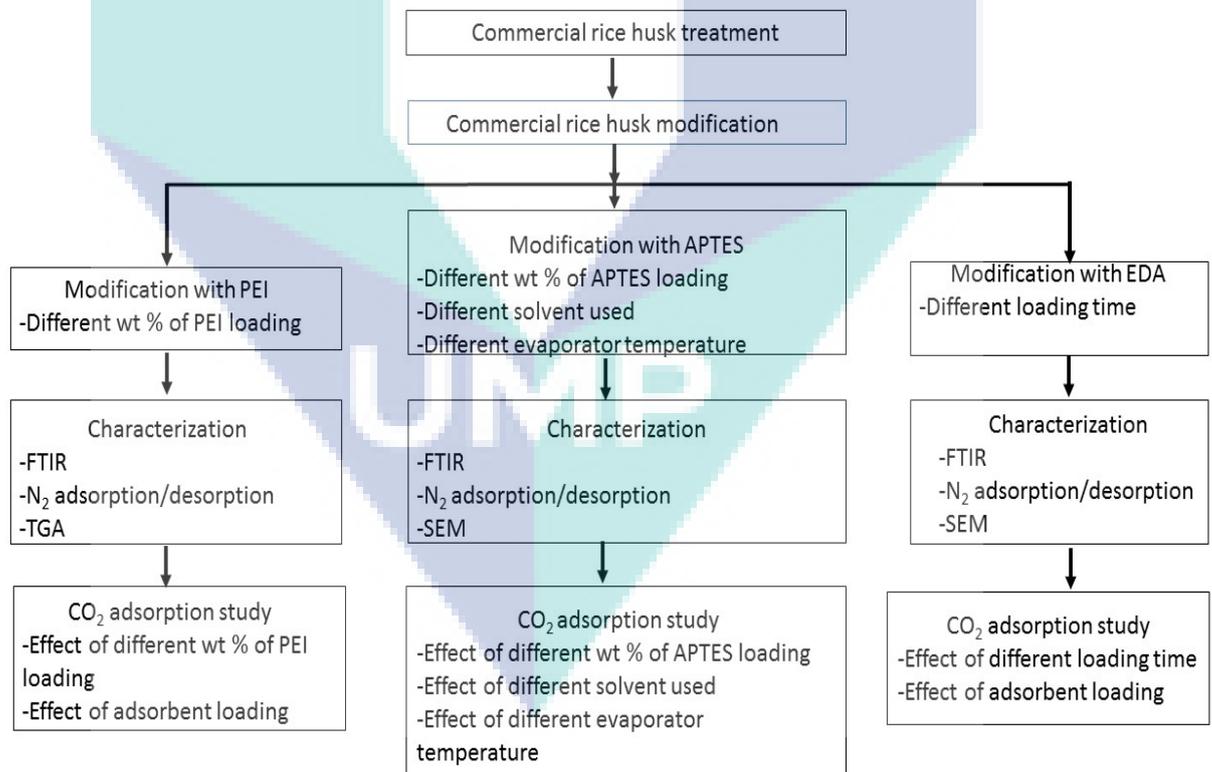


Figure 3. 1: Flow diagram of this research

## 3.2 Materials

All chemicals are listed in Table 3.1. All chemicals used were of analytical grade and were used as received without further purification.

Table 3. 1: List of chemicals used

Chemical/ Reagent	Supplier & Assay	Purpose of use
Commercial rice husk activated carbon	Sin Guan Hup Oil & Rice Mill Sdn Bhd, Penang	Adsorbent base
Polyethyleneimine (PEI) (MW=600000-1000000)		Modifying agent
Potassium hydroxide (KOH)		Modifying agent
3-aminopropyltriethoxysilane (APTES)		Modifying agent
Ethylenediamine (EDA)		Modifying agent
Ethanol		Solvent
Hydrochloride acid (HCl)		Additive

## 3.3 Adsorbent Synthesis and Modification

The commercial rice husk activated carbon (AC) was used as the base of the adsorbent. The AC went through pre-treatment first. Firstly, the AC was grinded to small particles and the AC particles's size was sifted using 500 nm sieve. Then, the AC was rinsed with deionized water followed by heating in oven at 70 °C for 6 hours. The sample was then kept in a dessicator at room temperature to avoid moisture effect. The modified AC was synthesized using four (4) types of chemicals which are polyethyleneimine (PEI), 3-aminopropyltriethoxysilane (APTES) and ethylenediamine (EDA). The method of modification was different for each chemical.

### 3.3.1 Modification with polyethyleneimine (PEI)

The modified AC was prepared based on different weight % (0.5, 1.0, 1.5 and 2.0) of PEI following the procedure reported elsewhere (Yin et al. 2007). In a typical preparation process, the required amount of PEI was mixed with 50 ml of DI water. Next,

the treated AC was mixed into the PEI solution and agitated in orbital shaker at 180 rpm at constant temperature of 25 °C for 5 hours. The impregnated AC was filtered and washed with DI water and the PEI-AC was obtained by drying in an oven at 60 °C for a day.

### **3.3.2 Modification with 3-aminopropyltriethoxysilane (APTES)**

The modified AC was prepared as per the reported procedure (Dali, A., Ibrahim, A. S., & Hadi 2012). Firstly, the mixture of AC and DI water with 10:1 solid/liquid weight ratio was stirred at 100 rpm. Then, the APTES was added to the mixture with different weight % (2,3,4 and 5) and sonicated for 10 minutes. The pH of suspension was adjusted to 3-4 using HCL solution. This solution was kept for 1 hour at room temperature and subsequently refluxed using an evaporator at different temperature (50, 70, 90 and 110 °C). The APTES-AC was obtained by vacuum-drying at 40 °C overnight.

### **3.3.3 Modification with ethylenediamine (EDA)**

The modified AC was prepared by refluxing 2 g rice husk activated carbon with 100 ml of EDA solution in different time (1, 2 and 4 hours) at 60 °C. This method was followed as reported by (Houshmand et al. 2013). The EDA-AC was obtained by filtered off, washed with DI water and oven dried at 80 °C for 8 hours.

## **3.4 Adsorbent Characterization**

The physiochemical and the morphology of the synthesized adsorbent were characterized using characterization equipment such as SEM, FTIR, N<sub>2</sub> adsorption/desorption analyzer and TGA.

### **3.4.1 Scanning Electron Microscope (SEM)**

SEM (JEOL JSM-7100F) instrument was used to determine the adsorbent morphology.

### 3.4.2 FTIR

The surface functional groups on the samples were identified using FTIR (Perkin Elmer Spectrum RX FTIR). The samples were mixed with KBr at ratio 5:95. The FTIR spectra were recorded within range  $400\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  wavelength.

### 3.4.3 N<sub>2</sub> adsorption/desorption analyzer

N<sub>2</sub> adsorption/desorption isotherms were measured at 77 K with a Quadrasorb SI analyser (Quantachrome, USA). The samples were degassed in vacuum at 373 K for 12 hours before the measurements. The specific surface area, pore size and pore volume were calculated using the Brunauer – Emmet- teller (BET) method.

### 3.4.4 TGA

TGA analysis was conducted using Mettler-Toledo TGA/SDTA851 Thermogravimetric Analyzer. It was performed to investigate the thermal behaviour of samples. The equipment was set to increase temperature from 20 °C to 700 °C at a rate of 10 °C/min under nitrogen atmosphere with a flow rate of 100 ml/min.

### 3.5 CO<sub>2</sub> Adsorption Activity

The CO<sub>2</sub> adsorption activity was carried out in a stainless steel adsorption column as shown in Figure 3.2. The adsorption column was packed with different PEI-AC and EDA-AC loading (0.5, 1, 1.5, 2.0 and 4.0 g) while APTES-AC were loaded at 10 g. The temperature was adjusted to 40 °C and the CO<sub>2</sub> gas was allowed to flow at 100 ml/min. The inlet and outlet gas concentration was measured using gas analyser. The dynamic adsorption capacity was calculated using Equation 3.1

$$Q = \frac{FC_o t_q}{W}$$

Equation 3.1

Where

$Q$  = adsorption capacity (mg/g)

$F$  = total molar flowrate of feed (mol/min)

$C_o$  = concentration of inlet stream

$W$  = weight of the solid adsorbent loaded in the column (g)

$t_q$  = stoichiometric time determined from the breakthrough curve via Polymath

Software by Equation 3.2.

$$t_q = \int_0^{\infty} \left(1 - \frac{C}{C_0}\right)$$

**Equation 3.2**

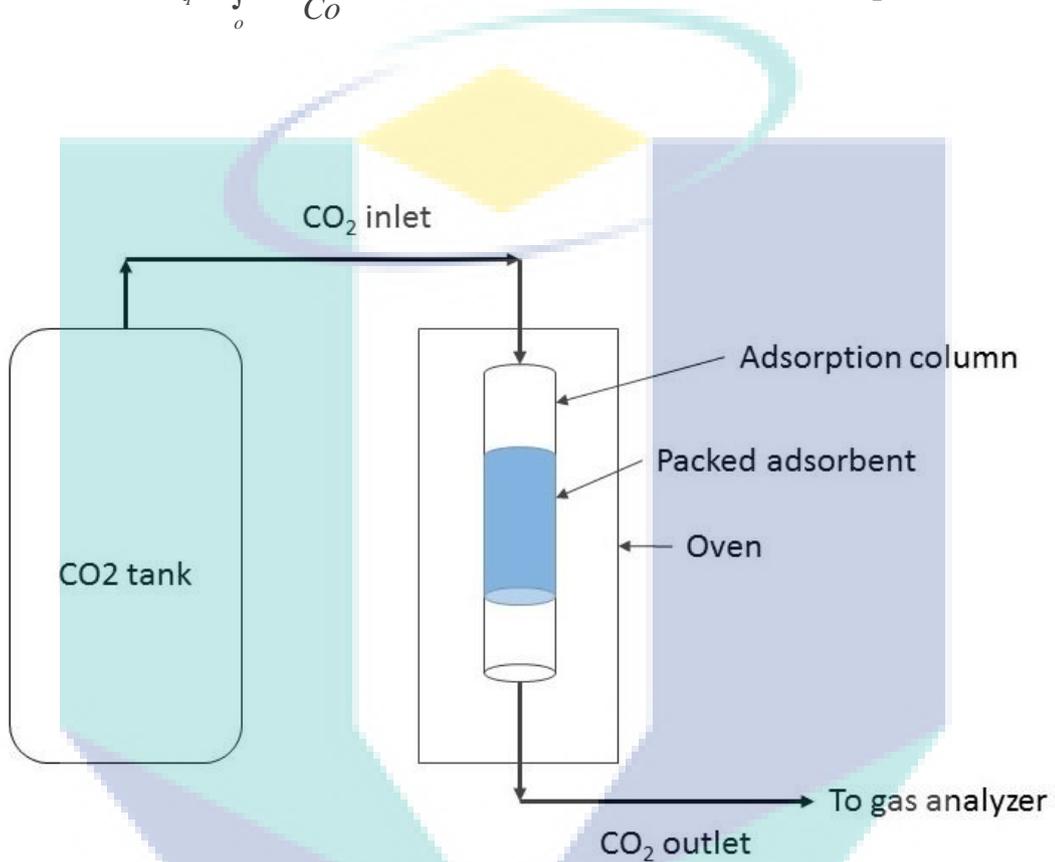


Figure 3. 2: Schematic diagram of experimental set up for CO<sub>2</sub> adsorption activity.

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Sample Characterization

##### 4.1.1 FTIR

###### 4.1.1.1 PEI-AC sample

The FTIR transmission spectra of raw and PEI-impregnated AC are shown in Figure 4.1. Triplicate spectra were obtained for each AC sample and they were all consistently similar. No significant peaking points are observed in all the samples and instead, peaks are present in forms of uniform elevations.

As shown in Figure 4.1, there are several bands appeared on the PEI-AC samples at  $1070\text{ cm}^{-1}$ ,  $1600\text{ cm}^{-1}$  and  $3450\text{ cm}^{-1}$ . The band at  $1070\text{ cm}^{-1}$  corresponds to the vibrational mode of epoxy groups (G. J. Shin, Rhee & Park 2016). A broad band in the region  $\sim 3450\text{ cm}^{-1}$  in both spectra may be assigned to  $\text{-OH}$  stretching vibrations mode of hydroxyl functional groups including hydrogen bonding of chemisorbed water or may be due to binding of  $\text{-OH}$  group with polymeric structure of rice husk (Chen et al. 2011a; G. J. Shin, Rhee & Park 2016). The peak at  $1600\text{ cm}^{-1}$  is the vibration of an amine group (Yin et al. 2007). Thus, the present of peak at  $1600\text{ cm}^{-1}$  indicates that the amine group of PEI had been successfully introduced onto AC surfaces which could generate new sites for  $\text{CO}_2$  adsorption. The comparison between the raw activated carbon with the modified activated carbon using PEI with different concentration shows new band appears on FTIR graph and confirmed the vibration of the amine group in PEI-AC. Other than that, the PEI-AC spectrum appears to be similar to the virgin AC spectra with no significant

deviations in absorbance. This suggest that the low adsorption of PEI does not have a significant effect on the surface chemistry of AC.

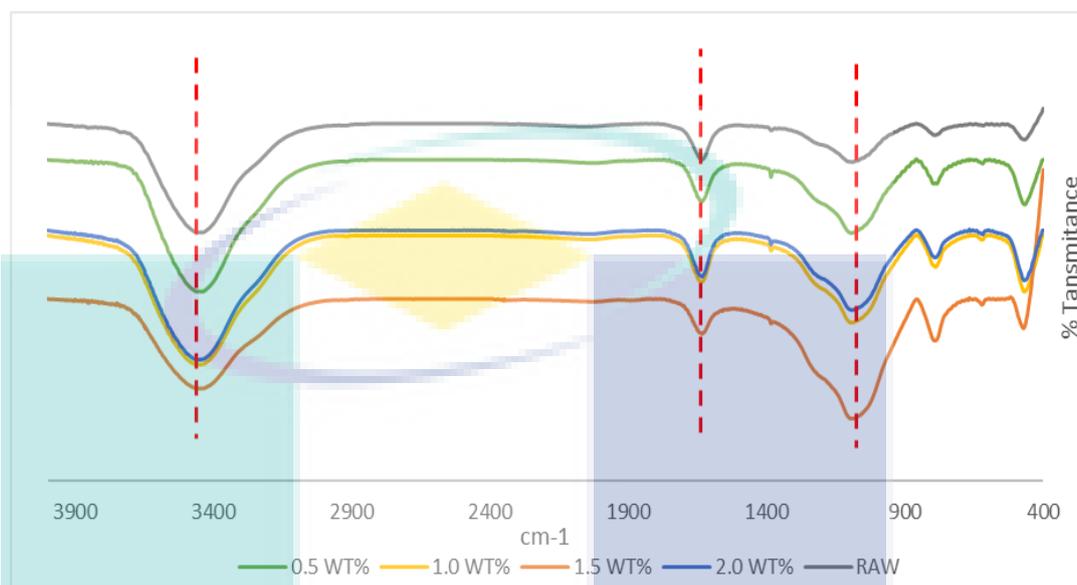


Figure 4. 1: FTIR of pure AC and PEI-AC with different weight % PEI loading

#### 4.1.1.2 APTES-AC sample

Figure 4.2 shows the FTIR results of pure activated carbon (AC) and AC-APTES with different weight % APTES. It was observed that the pattern of the AC-APTES almost same as pure AC. However, there are several new bands appeared on the AC-APTES samples at  $1630\text{ cm}^{-1}$  and  $3251\text{ -}3558\text{ cm}^{-1}$ . The peak at  $1630\text{ cm}^{-1}$  is the vibration of an amine group (Zhang et al. 2014). Thus, the present of peak at  $1630\text{ cm}^{-1}$  indicates that the amine groups of APTES had been successfully introduced onto AC surfaces which could generate new sites for  $\text{CO}_2$  adsorption. The comparison between the raw activated carbon with the modified activated carbon using APTES with different concentration shows new band appears on FTIR graph and confirmed the vibration of the amine group in APTES-AC. For sample 2 %, 3 %, 4 % shows there is new bands at  $1630\text{ cm}^{-1}$  while for a 5 % sample there is no difference with raw AC. So, the sample 5 % failed to interact in the body of activated carbon. The 4% sample shows the highest peak of vibration which shows the interaction between APTES with AC is very strong. The vibration of the amine group in APTES-AC usually shows bands at  $1750\text{ -}1620\text{ cm}^{-1}$  (Zhang et al. 2014). The water plays a catalytic role for the hydrolysis of AC surface and demonstrated that amine

groups of APTES had been successfully introduced onto AC surfaces which would generate new sites for CO<sub>2</sub> adsorption.

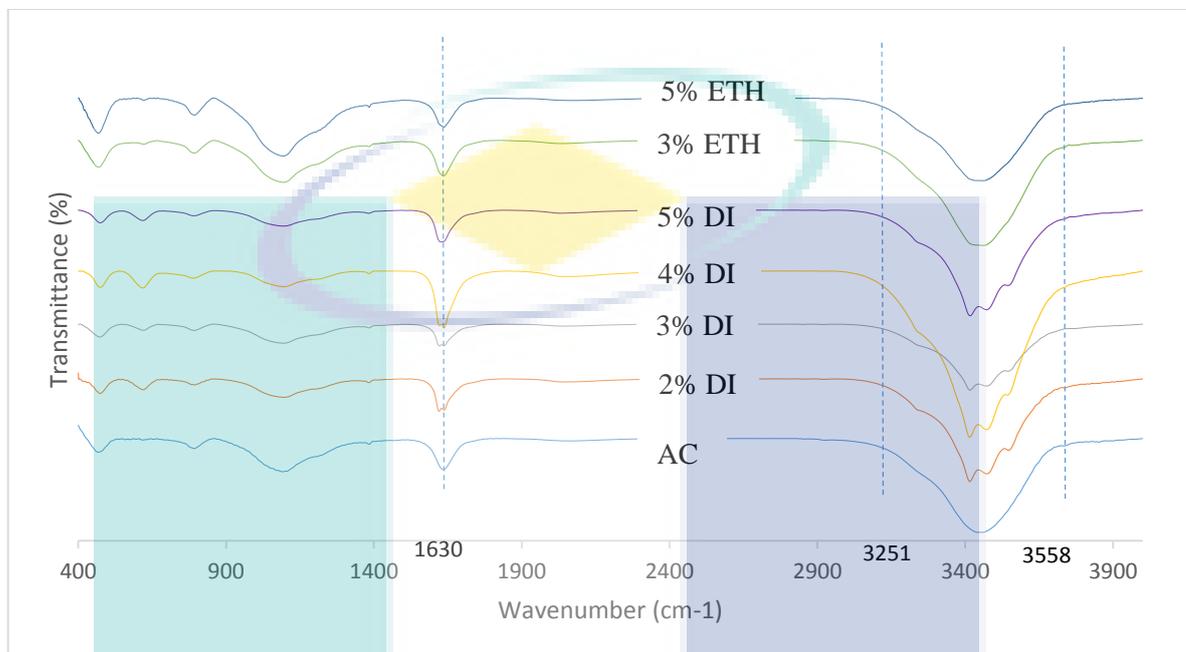


Figure 4. 2: FTIR of pure AC and APTES-AC with different weight % APTES loading and different solvent

#### 4.1.1.3 EDA-AC sample

The FTIR transmission spectra of raw and EDA impregnated AC are shown in Figure 4.3. Triplicate spectra were obtained for each AC sample and they were all consistently similar. No significant peaking points are observed in all the samples and instead, peaks are present in forms of uniform elevations.

As shown in Figure 4.3, significant differences are present in the spectra of raw AC and modified EDA-AC. There are several bands appeared on the EDA-AC samples at 1090 cm<sup>-1</sup>, 1650 cm<sup>-1</sup> and 3450 cm<sup>-1</sup>. The band at 1090 cm<sup>-1</sup> corresponds to the vibrational mode of epoxy groups (G.-J. Shin, Rhee & Park 2016). A broad band in the region 3000-3500 cm<sup>-1</sup> in both spectra may be assigned to -OH stretching vibrations mode of hydroxyl functional groups including hydrogen bonding of chemisorbed water or may be due to binding of -OH group with polymeric structure of rice husk (Chen et al. 2011a; G.-J. Shin et al. 2016). There was new strong absorption peak at 1650 cm<sup>-1</sup> which

indicated the vibration of an amine group (Dong et al. 2010). Thus, the present of peak at  $1650\text{ cm}^{-1}$  indicates that the amine group of EDA had been successfully introduced onto AC surfaces. The comparison between the raw AC with the modified AC using EDA with different loading time shows new band appears on FTIR graph and confirmed the vibration of the amine group in EDA-AC.

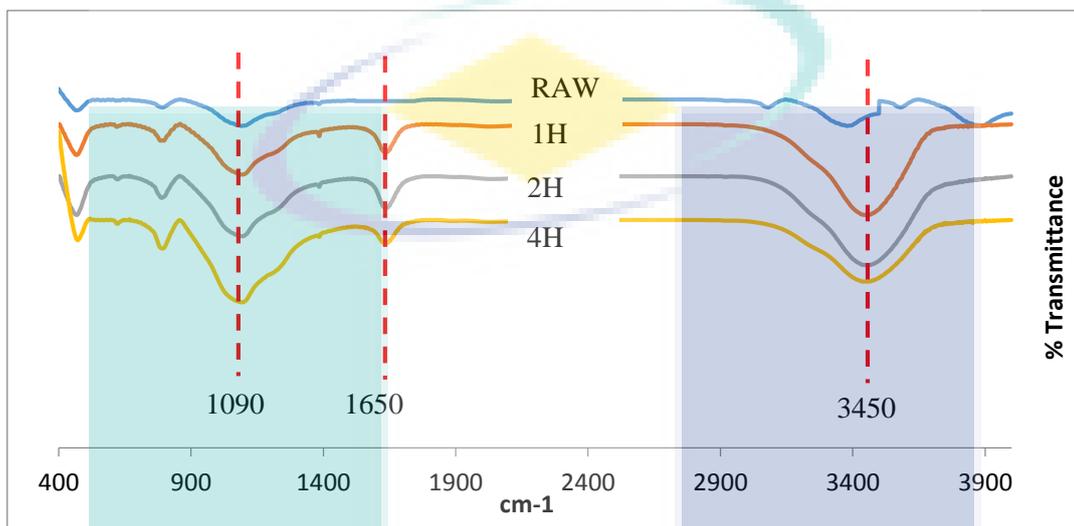


Figure 4. 3: FTIR of raw AC and EDA-AC with different EDA loading time

#### 4.1.2 $\text{N}_2$ adsorption/desorption analyzer

##### 4.1.2.1 PEI-AC sample

The BET surface area of the AC samples are shown in Table 4.1. The raw AC possessed a high BET surface area of  $52.5446\text{ m}^2/\text{g}$ . The BET surface area after being impregnated with 0.5 wt% of PEI is  $20.3607\text{ m}^2/\text{g}$  which has the smallest surface area compared to the rest of the sample. The decreased in the BET surface area of 0.5 wt% PEI-AC sample can be attributed to the blockage of pore after functionalization of polyethyleneimine. This confirmed that PEI was successfully introduced into the channels of the support (Wang et al. 2013). The increase of percentage PEI impregnation reduces the BET surface area for a particular type of PEI implying that higher quantity of PEI in bulk solution promotes higher adsorption on the surface of the AC resulting in decrease of free surface area. It is strongly suggested that this is due to two factors: (1) volume filling of PEI molecules into micropores, rendering blockage of the pores and (2) reduction and constriction of pore size (diameter) of macropores as a result of adsorbed PEI molecules on their walls (Yin et al. 2008). The first factor is construed as more dominant as macropores are usually present in small quantity. The BET surface area then

increased with increasing PEI loading. This is because the PEI molecules are deemed too large to infiltrate smaller micropores. Therefore, volume filling of micropores with PEI molecules is construed as insignificant (Yin et al. 2008).

Table 4.1: BET surface area for PEI-AC samples

Sample	BET Surface Area (m <sup>2</sup> /g)
Raw AC	52.5446
0.5 wt% PEI-AC	20.3607
1.0 wt% PEI-AC	40.2127
1.5 wt% PEI-AC	53.3491
2.0 wt% PEI-AC	54.2988

#### 4.1.2.2 APTES-AC sample

Table 4.2 shows the result for BET surface area for APTES-AC samples. BET surface area for 5% concentration of APTES use of modified activated carbon with ethanol solvent shows the higher 77.9575 m<sup>2</sup>/g while the lowest at 5% concentration of APTES use of modified activated carbon which is 50.4551 m<sup>2</sup>/g. Comparing between raw activated with modified one shows there is increasing on surface area for the modified activated carbon while comparing with different solvent also shows solvent ethanol shows the higher BET surface area compare with solvent water uses. The BET surface area is ranked as follows: 5 % AC-APTES-DI < AC < 2 % AC-APTES-DI < 3 % AC-APTES-DI < 3 % AC-APTES-Ethanol < 4 % AC-APTES-DI < 5 % AC-APTES-Ethanol. The highest the BET surface area will make the higher adsorption capacity for activated carbon to adsorb CO<sub>2</sub>.

Table 4.2: BET surface area for APTES-AC samples

Sample	Solvent	BET Surface Area (m <sup>2</sup> /g)
Raw AC	-	52.5446
2 wt% APTES-AC	DI water	55.0835
3 wt% APTES-AC		59.7202
4 wt% APTES-AC		74.9432

5 wt% APTES-AC		50.4551
3 wt% APTES-AC		70.6582
5 wt% APTES-AC	Ethanol	77.9575

#### 4.1.2.3 EDA-AC sample

The BET surface areas of the EDA-AC samples are shown in Table 4.3. The raw AC possessed a high BET surface area of 52.5446 m<sup>2</sup>/g. Comparing between raw AC with modified EDA-AC shows there were decreased on surface area for the modified AC. The BET surface area of AC after being impregnated with EDA for 2H is 9.8610m<sup>2</sup>/g which has the smallest surface area compared to the rest of the samples. The surface area decreased initially, reached minimum at 2H and then increased. The surface area of EDA-AC at 2H reached the minimum value due to sufficient contact time for the EDA and AC. Impregnation of amine groups causes a drastic decrease in surface area and pore volume. The decreased in the BET surface area of EDA-AC at 2H sample can be attributed to the blockage of pore after functionalization of ethylenediamine or destructions of pore walls (Houshmand et al. 2013). This confirmed that EDA was successfully introduced into the channels of the support (Wang et al. 2013). According to (Yin et al. 2008), the increase of percentage EDA impregnation reduces the BET surface area for a particular type of EDA implying that higher quantity of EDA in bulk solution promotes higher adsorption on the surface of the AC resulting in decrease of free surface area. It is strongly suggested that this is due to two factors: (1) volume filling of EDA molecules into micropores, rendering blockage of the pores and (2) reduction and constriction of pore size (diameter) of macropores as a result of adsorbed EDA molecules on their walls.

Table 4.3: BET surface area for EDA-AC samples

Sample	BET Surface Area (m <sup>2</sup> /g)
Raw AC	52.5446
EDA-AC (1 hour)	11.0590
EDA-AC (2 hours)	9.8610
EDA-AC (3 hours)	11.5293

### 4.1.3 TGA

#### 4.1.3.1 PEI-AC sample

TG analysis was performed to investigate the thermal behaviour of virgin and PEI-impregnated AC. Based on Figure 4.4, the virgin AC experiences an observable increased weight loss up to 100 °C due to vaporization of physically adsorbed water. This is due to the thermodesorption of surface oxides which evolved CO<sub>2</sub> gas and water vapour.

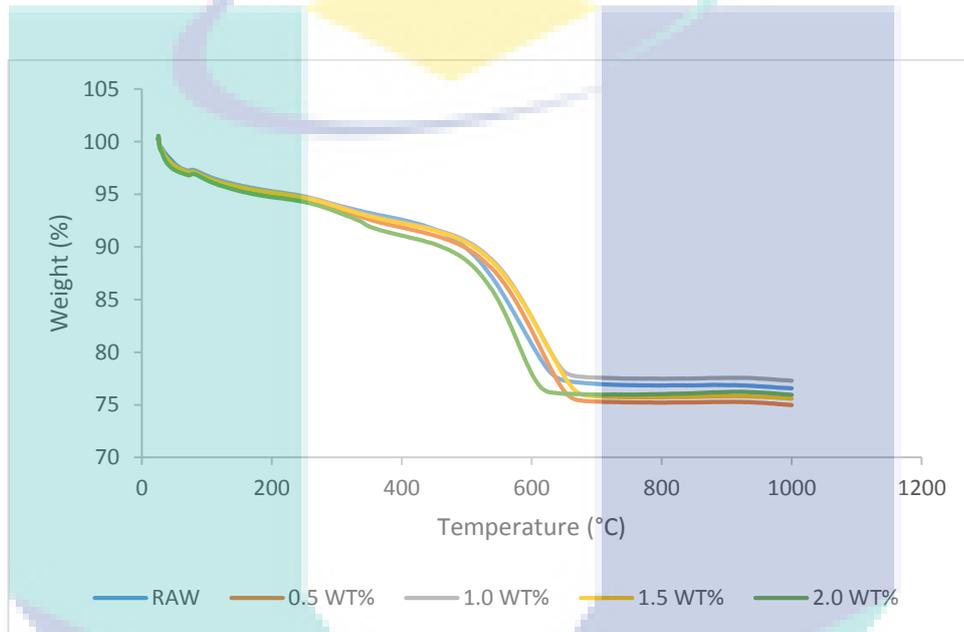


Figure 4. 4: TGA curves of the AC with different PEI loadings

The pure PEI started to decompose at 200°C and finished at 400°C (Wang et al. 2013). The decomposition products were completely released as gases. For the PEI-loaded sorbents, the decomposition temperature apparently decreased by 50°C. From Figure 4.2, it is observed that PEI-impregnation results in lower weight losses as compared to virgin AC. This indicates that PEI-impregnation may have thermally stabilizes the AC. This observation implies that relatively higher resistance to thermal elevations (>100 °C) exhibited by the PEI-impregnated AC indicates that it can be favourable in removing CO<sub>2</sub> in high temperature gas streams in the oil and gas industry.

The trend in which decreases in weight for all samples at elevated temperature observed in this study was in contrast with the study conducted by El-Sayed and Badosz in which they found that coal and wood based AC samples (virgin, ethylmethyamine-impregnated or oxidized) experienced weight gains from 400 °C onwards. They pointed

out that this anomaly indicated incorporation of nitrogen into the carbon matrix (Yin et al. 2007).

#### 4.1.4 SEM

##### 4.1.4.1 APTES-AC sample

As shown in Figure 4.5, there is obvious morphological differences of the SEM micrographs between AC, AC-APTES-Water and AC-APTES-Ethanol. The sample modified with APTES in water and toluene solvent shows bigger pore size compared than unmodified AC at a same temperature process. AC had many microspores on its surface (Fig. 4.5 (a)). After being modified using APTES we can see the microspores were generated and become more depends with AC as shown in (Fig. 4.5 (b)). Surface morphology shows more development or generation of a lot of microporous on surface body of the AC-APTES-Ethanol as shown in (Fig. 4.5 (c)). By comparing these three figures, we can conclude that the modified activated carbon shows a lot of different with a lot of new microspores generated at the surface body activated carbon. We also can compare between solvent used also affected the generation of the microspores on the body of activated carbon. Solvent ethanol shows more affective because the size and numbers of microspores are more (Fig. 4.5 (c)) compare with solvent water (Fig. 4.5 (b)) at 3% of APTES. However, based on (Przepiórski, Skrodzewicz & Morawski 2004), at high concentration of amine solvent, the pore size of adsorbent will be decrease which it may cause by closing of microspores entries by N-containing groups.

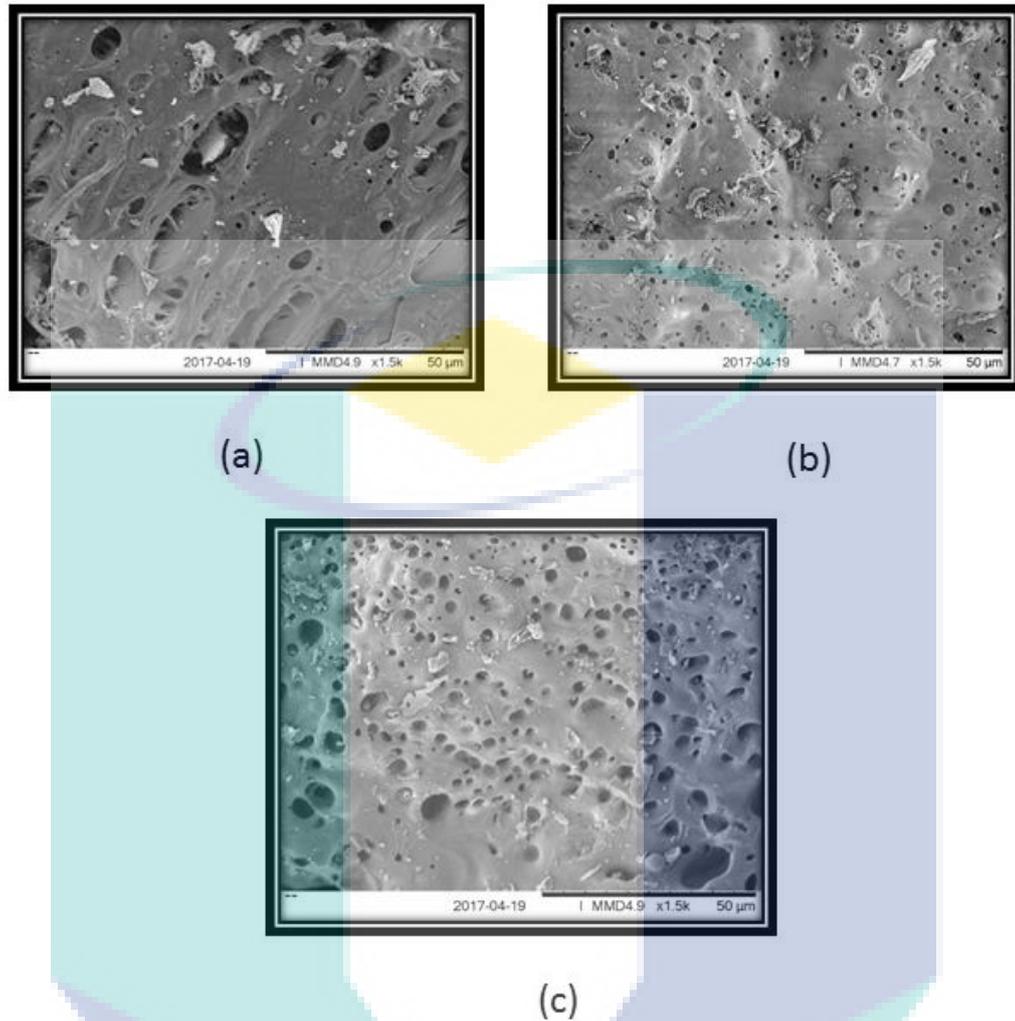


Figure 4. 5: SEM of: (a) the Raw rice husk activated carbon (AC); (b) Modified rice husk using 3% APTES with DI water solvent (MAC-DI); (c) Modified rice husk using 3% APTES with Ethanol solvent (MAC-ETH).

#### 4.1.4.2 EDA-AC sample

From Figure 4.6, there are an obvious morphological difference of the SEM micrographs between AC and EDA-AC. After being modified using EDA, the thick wall gets opened and a wider porosity is created, as can be seen in Figure 4.6 (b) that their images consist of more pores and channels than the raw AC. Moreover, it can be seen the micropores were generated and become more depends with AC as shown in Figure 4.6 (b). Surface morphology shows more development or generation of a lot of microporous on surface body of the EDA-AC. By comparing these figures, it can be concluded that the modified AC shows a lot of different with a lot of new micropores generated at the surface body of AC. The porous structures of modified AC may result from the bridging linkage of EDA molecules among the amine groups in the modified AC surface through

the intra- and/or inter-molecular cross linking connections, which may generate new binding sites in interior walls of the micropores (Zhu, Yang & Deng 2009).

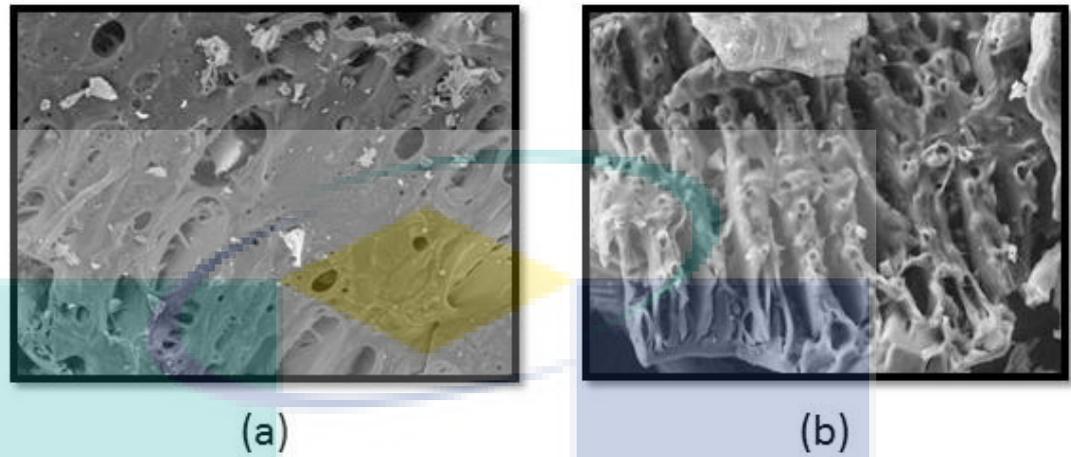


Figure 4. 6: (a) Raw rice husk activated carbon (AC); (b) EDA modified activated carbon (EDA-AC)

## 4.2 CO<sub>2</sub> Adsorption Activity

### 4.2.1 PEI-AC sample

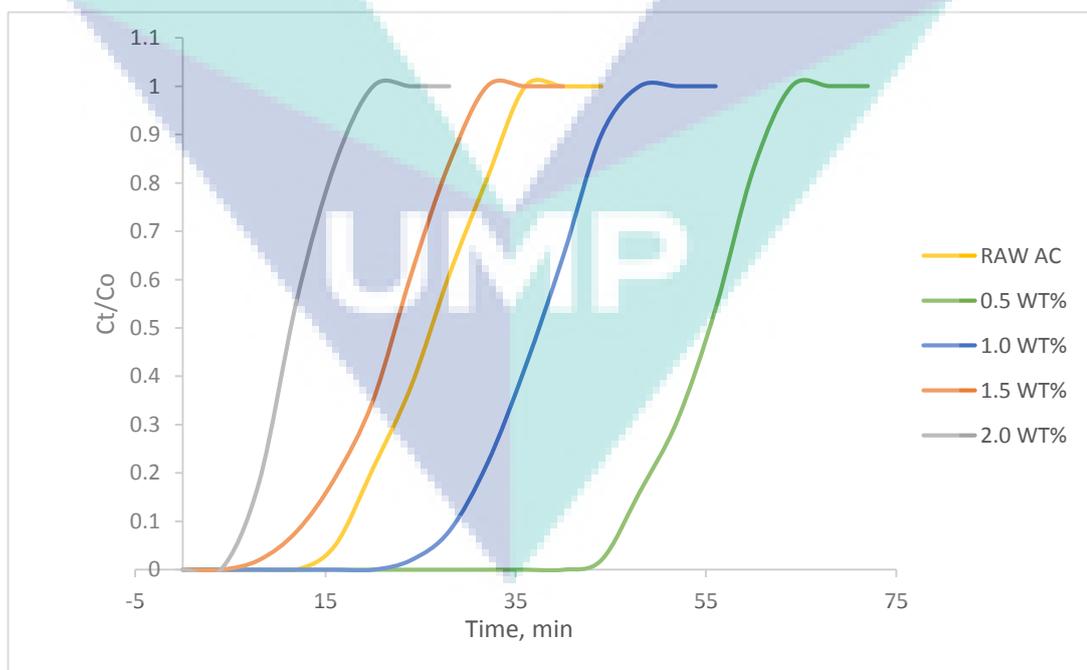


Figure 4. 7: CO<sub>2</sub> adsorption performance with different PEI-AC samples

Table 4.4: Adsorption capacity at breakthrough time for modified AC with different PEI-AC samples

Sample	Adsorption Capacity (g/g)
AC	0.11
0.5 wt% PEI-AC	0.24
1.0 wt% PEI-AC	0.16
1.5 wt% PEI-AC	0.09
2.0 wt% PEI-AC	0.05

The CO<sub>2</sub> sorption breakthrough curves of the sorbents with different PEI loadings are shown in Figure 4.7. The sorption rate is rapid at the beginning phase, as shown by the approximately zero CO<sub>2</sub> concentration of the effluent gas. The breakthrough curves become sharper as the PEI loading decrease.

The saturation sorption capacities at dynamic conditions of the sorbents were calculated and summarized in Table 4.4. The raw AC exhibited a negligible adsorption capacity (0.11 g/g), due to the limited physisorption of CO<sub>2</sub> on this material. After the impregnation with PEI, the adsorption capacity increased and achieved a maximum at 0.5 wt% PEI loading. The largest adsorption capacity developed in this work was 0.24 g/g, which is significantly higher than that of 1.0 wt% PEI-AC (0.16 g/g). When the PEI loading further increased at 1.0 wt%, the adsorption capacity later on decrease. This is attributed to excessive overloaded polyethylenimine being impregnated on the activated carbon surface. When the polyethyleneimine was overloaded onto the surface of adsorbents, it resulted in decreasing CO<sub>2</sub> adsorption capacity. When extra polyethyleneimine covers the outer surface of PEI-AC, resulting in more agglomeration and diffusional resistance, the accessible sorption site is reduced (Liu et al. 2015a).

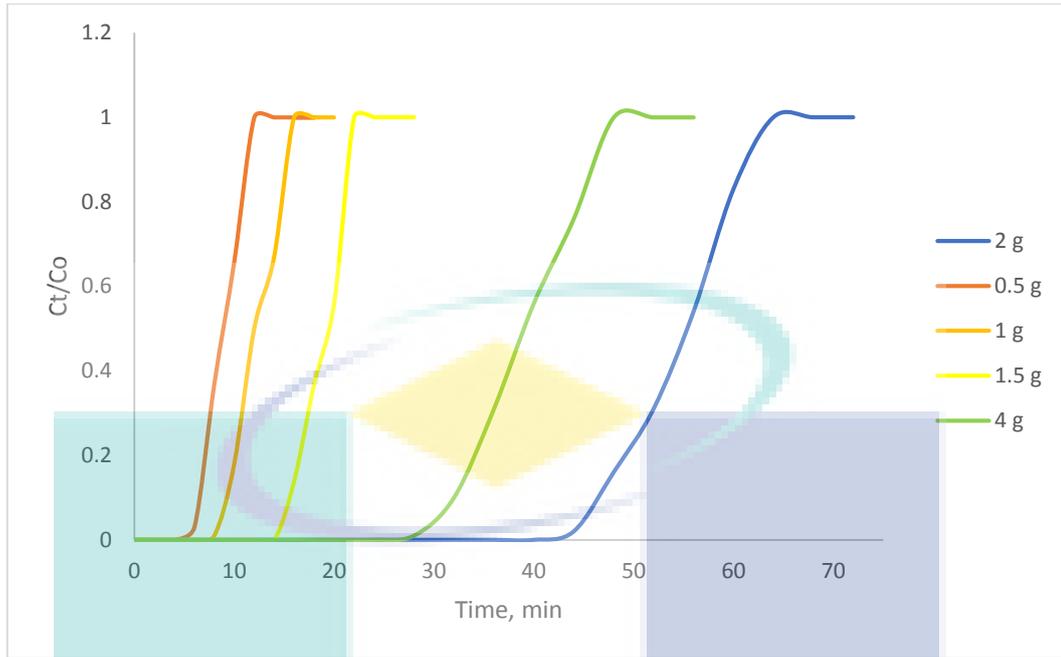


Figure 4. 8: CO<sub>2</sub> adsorption performance with different 0.5 wt% PEI-AC loading

Table 4.5: Adsorption capacity at breakthrough time for modified AC with different 0.5 wt% PEI-AC loading

Adsorbent Loading	Adsorption Capacity (g/g)
0.5 g	0.04
1.0 g	0.05
1.5 g	0.08
2.0 g	0.24
4.0 g	0.17

Figure 4.8 shows the breakthrough curve obtained for PEI-AC adsorption on the prepared activated carbon for 5 different adsorbent weight loading of 0.5, 1.0, 1.5, 2.0 and 4.0 g, at a constant flow rate of 100 mL/min and PEI loading of 0.5 wt%. Increasing the weight loading meaning that the adsorbent bed height to be increased. The breakthrough increased with increasing the bed height. It is known that specific surface area and fixable binding sites for adsorbate is increased with increase in the adsorbent bed height thereby leading to more volume of effluent gas treatment as a result of larger service area provided (Auta, & Hameed 2014). In this research, it was seen that the adsorption capacity increased with increasing bed height. (I. A. W. Tan, Ahmad & Hameed 2008) reported in their work that when the bed height was reduced, axial dispersion phenomena predominated in the mass transfer and reduced the diffusion of the

solute, and therefore the solute had not enough time to diffuse into the whole of the adsorbent mass.

#### 4.2.2 APTES-AC sample

The CO<sub>2</sub> adsorption capacity and the surface area for all samples is tabulated in Table 4.6. It shows that the adsorption capacity for AC samples is 1.69 g/g. Loading 2 % APTES onto AC just small increase the adsorption capacity to 1.74 g/g. The adsorption capacity was increased after loading 3 % APTES and decreases after loading 5 % APTES. It shows that there is an optimum APTES loading which is 4 % APTES. The BET surface area loading 5 % APTES decrease 4% relative to the initial activated carbon. This happens because pore blockage in microspores so it is leading to a decrease in adsorption capacity. The adsorption performances are ranked as follows: 5 % AC-APTES < AC < 2 % AC-APTES < 3 % AC-APTES < 4 % AC-APTES. This result was attributed from a chemical reaction of APTES, adsorbent AC and CO<sub>2</sub>. The higher adsorption performance of modified AC than pure AC indicating the good role of chemisorption in adsorption process occurred. According to (Plaza et al. 2007), the amine coating increased the basicity and nitrogen content of the carbon. But, if higher when the higher concentration of amine used, it can drastically reduce the microporous volume of the AC which is responsible for CO<sub>2</sub> physisorption. Thus, decreasing the capacity of CO<sub>2</sub> adsorption.

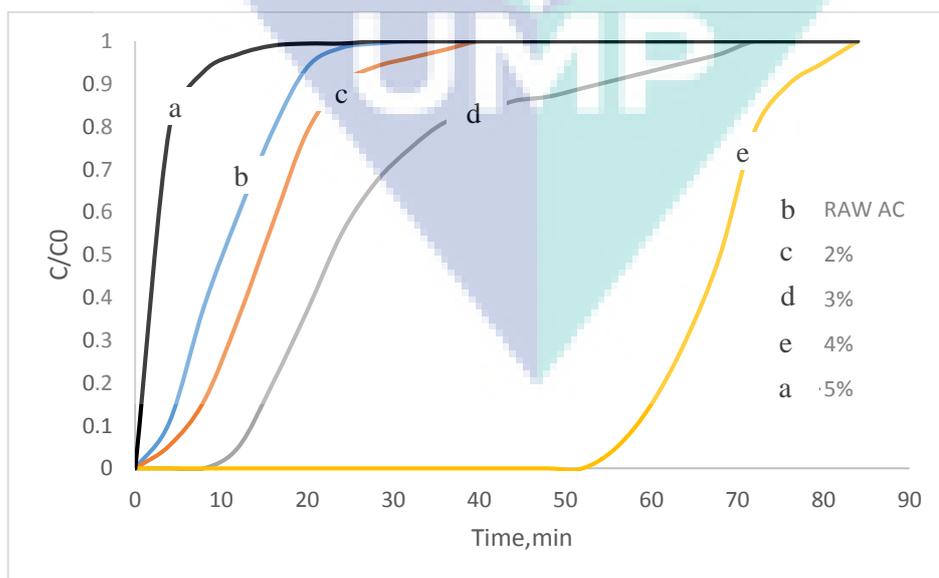


Figure 4. 9: CO<sub>2</sub> adsorption performance with different wt % APTES modified activated carbon using DI water solvent.

Table 4.6: Adsorption capacity at breakthrough time for APTES-AC samples using DI water as solvent

Sample	Adsorption Capacity (g/g)
AC	1.69
2 wt % APTES-AC	1.74
3 wt % APTES-AC	5.22
4 wt % APTES-AC	24.38
5 wt % APTES-AC	1.07

Adsorption capacity for modified activated carbon with different evaporator temperature does not enhance the ability of rice husk activated carbon to adsorb CO<sub>2</sub> as shown in Figure 4.10 and Table 4.7. The adsorption capacity compares with unmodified rice husk activated carbon does not much different.

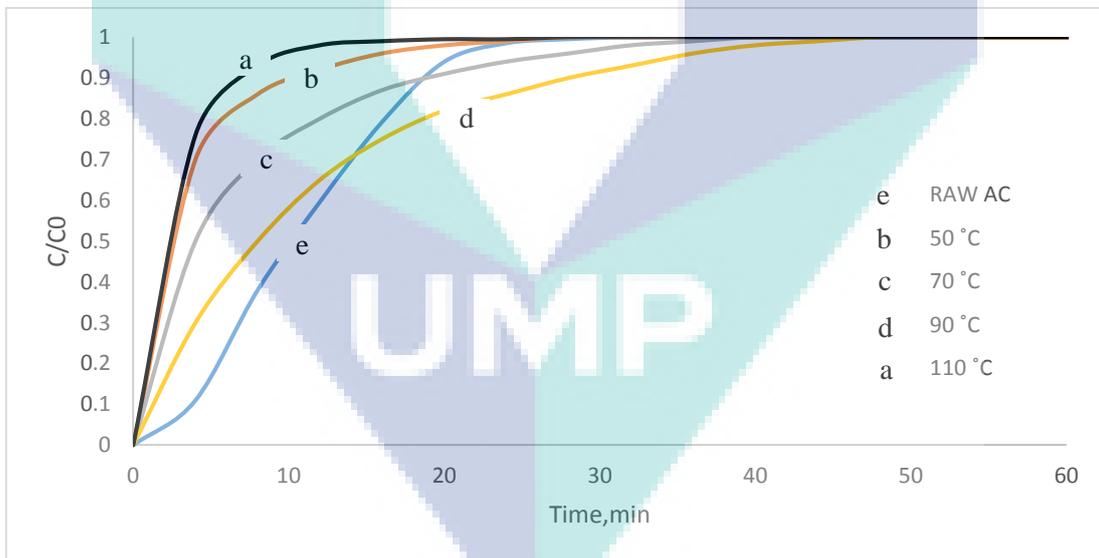


Figure 4.10: CO<sub>2</sub> adsorption performance of 4 wt % APTES-AC using DI water as solvent with different evaporator temperature

Table 4.7: Adsorption capacity at breakthrough time for 4 wt % APTES-AC using DI water as solvent with different evaporator temperature

Sample	Adsorption Capacity (g/g)
AC	1.69
APTES-AC (50 °C)	1.16
APTES-AC (70 °C)	1.34
APTES-AC (90 °C)	1.52
APTES-AC (110 °C)	1.11

By comparing adsorption capacity for modified activated carbon using solvent ethanol with water shows that solvent modified activated carbon using ethanol solvent gives better result as shown in Figure 4.11 and Table 4.8. The highest adsorption capacity happens at 5 wt % APTES which is 76.02 g/g compare to water solvent only 24.34 g/g. According to (Przepiórski et al. 2004), the higher adsorption capacity of modified AC was contributed from the presence of the C-N group introduced to the carbon structure during modification. The chemisorption from APTES interaction with adsorbent AC help increase the efficiency of physisorption of CO<sub>2</sub>.

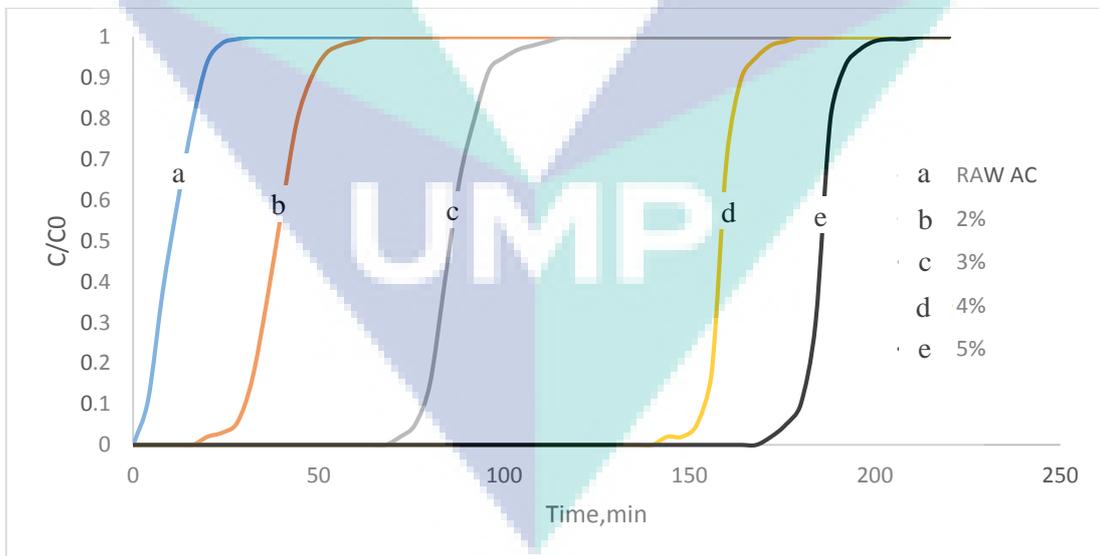


Figure 4.11: CO<sub>2</sub> adsorption performance with different wt % APTES modified activated carbon using ethanol as solvent.

Table 4.8: Adsorption capacity at breakthrough time for APTES-AC samples using ethanol as solvent

Sample	Adsorption Capacity (g/g)
AC	1.69
2 wt % APTES-AC	8.84
3 wt % APTES-AC	31.82
4 wt % APTES-AC	63.64
5 wt % APTES-AC	76.02

Adsorption capacity for modified activated carbon with different evaporator temperature does not enhance the ability of rice husk activated carbon to adsorb CO<sub>2</sub> as shown in table 4.2.2.2. The adsorption capacity compares with unmodified rice husk activated carbon does not much different.

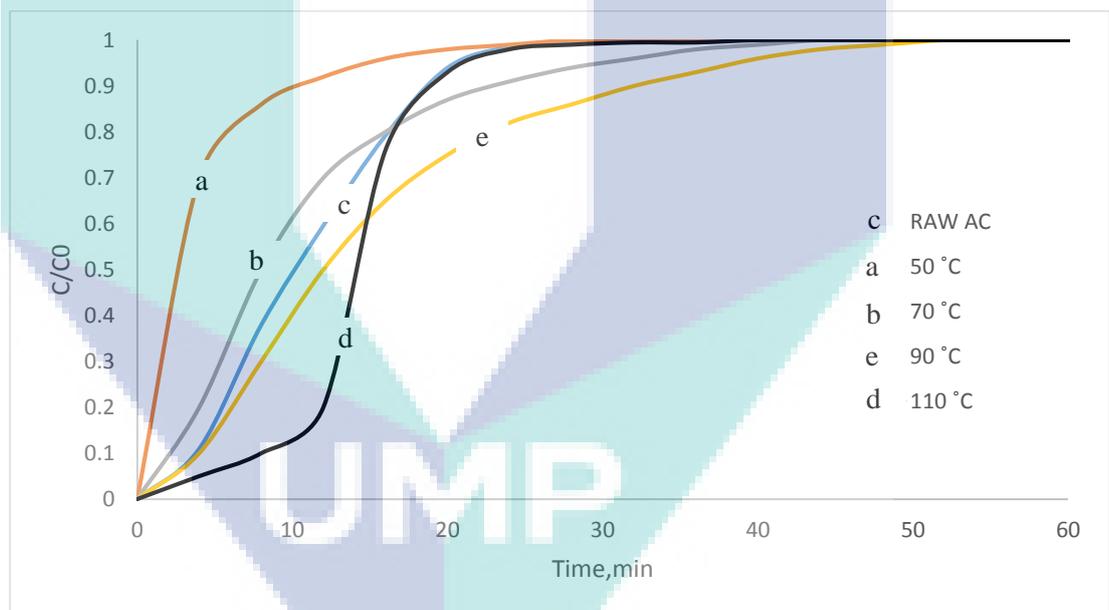


Figure 4.12: CO<sub>2</sub> adsorption performance of 5 wt % APTES-AC using ethanol as solvent with different evaporator temperature

Table 4.9: Adsorption capacity at breakthrough time for 5 wt % APTES-AC using ethanol as solvent with different evaporator temperature

Sample	Adsorption Capacity (g/g)
AC	1.69
APTES-AC (50 °C)	1.16
APTES-AC (70 °C)	1.61
APTES-AC (90 °C)	1.70
APTES-AC (110 °C)	1.74

#### 4.2.3 EDA-AC sample

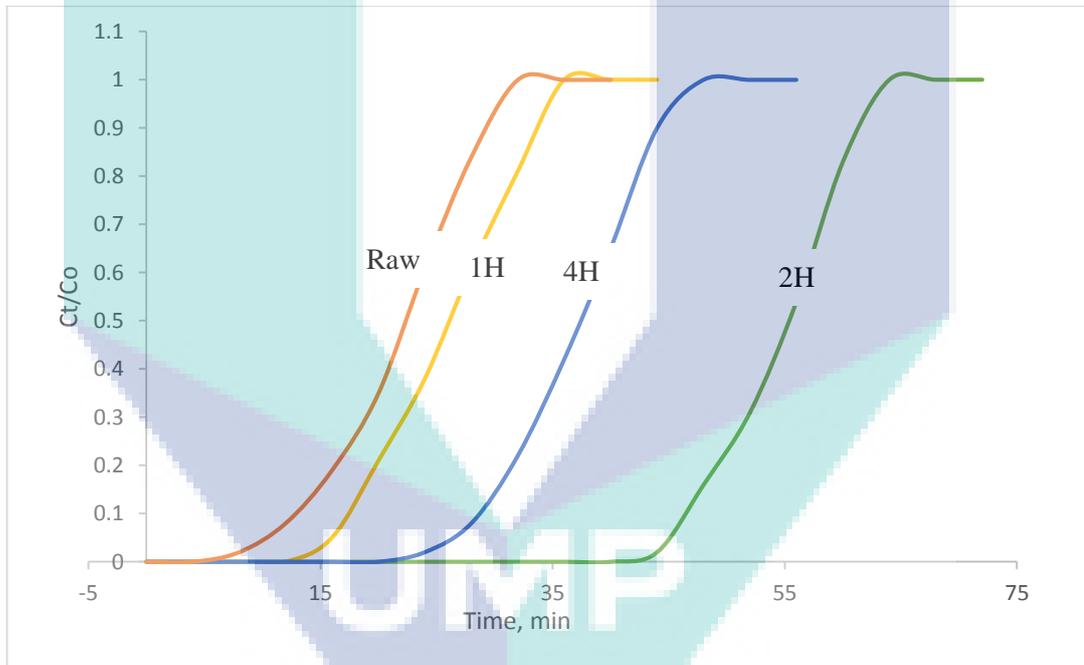


Figure 4. 13: CO<sub>2</sub> adsorption performance with different EDA-AC samples

Table 4.10: Adsorption capacity at breakthrough time for different EDA-AC samples

Sample	BET Surface Area (m <sup>2</sup> /g)
Raw AC	0.08
EDA-AC (1 hour)	0.10
EDA-AC (2 hours)	0.20
EDA-AC (3 hours)	0.14

The CO<sub>2</sub> adsorption breakthrough curves of the adsorbents with different EDA loading time and adsorption capacity are shown in

Figure 4. **13**: CO<sub>2</sub> adsorption performance with different EDA-AC samples

Table 4.10: Adsorption capacity at breakthrough time for different EDA-AC samples

and Table 4.10, respectively. It shows that the adsorption capacity for AC samples is 0.08 g/g due to the limited physisorption of CO<sub>2</sub> on this material. Loading EDA onto AC for 1 hour showed just small increase in the adsorption capacity to 0.10 g/g. The largest adsorption capacity developed in this work was 0.20 g/g, which is significantly higher than that of EDA-AC (3 hours) sample (0.14 g/g). The adsorption capacity was increased after loading EDA for 2 hours and achieved a maximum at 2 hours then decreased after loading EDA for 3 hours. It shows that there is an optimum EDA loading time which is 2 hours. The decreased surface area of BET EDA-AC (2 hours) shows that the EDA successfully introduced onto the AC surface. The impregnation of large amounts of amines on the micropores of AC attributes to high adsorption capacity in relation to CO<sub>2</sub> (Boonpoke et al. 2011).

The higher adsorption performance of modified AC than raw AC indicating the good role of chemisorption in adsorption process occurred. The amine coating increased the basicity and nitrogen content of the carbon (Plaza et al. 2007). When the EDA loading time further increased to 3 hours the adsorption capacity later on decreased. This is attributed to excessive overloaded EDA being impregnated on the activated carbon surface, where it can drastically reduce the microporous volume of the AC which is responsible for CO<sub>2</sub> physisorption. When the EDA was overloaded onto the surface of adsorbents, it resulted in decreasing CO<sub>2</sub> adsorption capacity. When extra EDA covers the outer surface of modified AC, resulting in more agglomeration and diffusional resistance, thus decreasing the capacity of CO<sub>2</sub> adsorption (Liu et al. 2015b). For an example, according to (Plaza et al. 2007), when higher concentration of amine used, it can drastically reduce the microporous volume of the AC which is responsible for CO<sub>2</sub> physisorption. Thus, decrease the capacity of CO<sub>2</sub> adsorption. Moreover, (Przepiórski et al. 2004) stated that the higher adsorption capacity of modified AC was contributed from the presence of the C-N group introduced to the carbon structure during modification.

The chemisorption from EDA interaction with adsorbent AC helps increase the efficiency of physisorption of CO<sub>2</sub>.

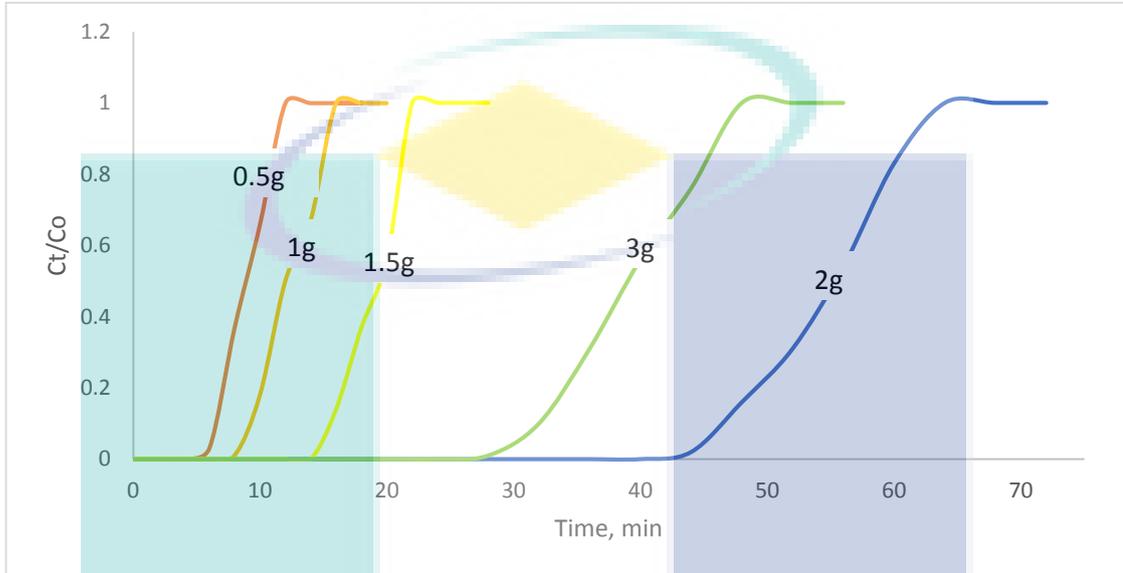


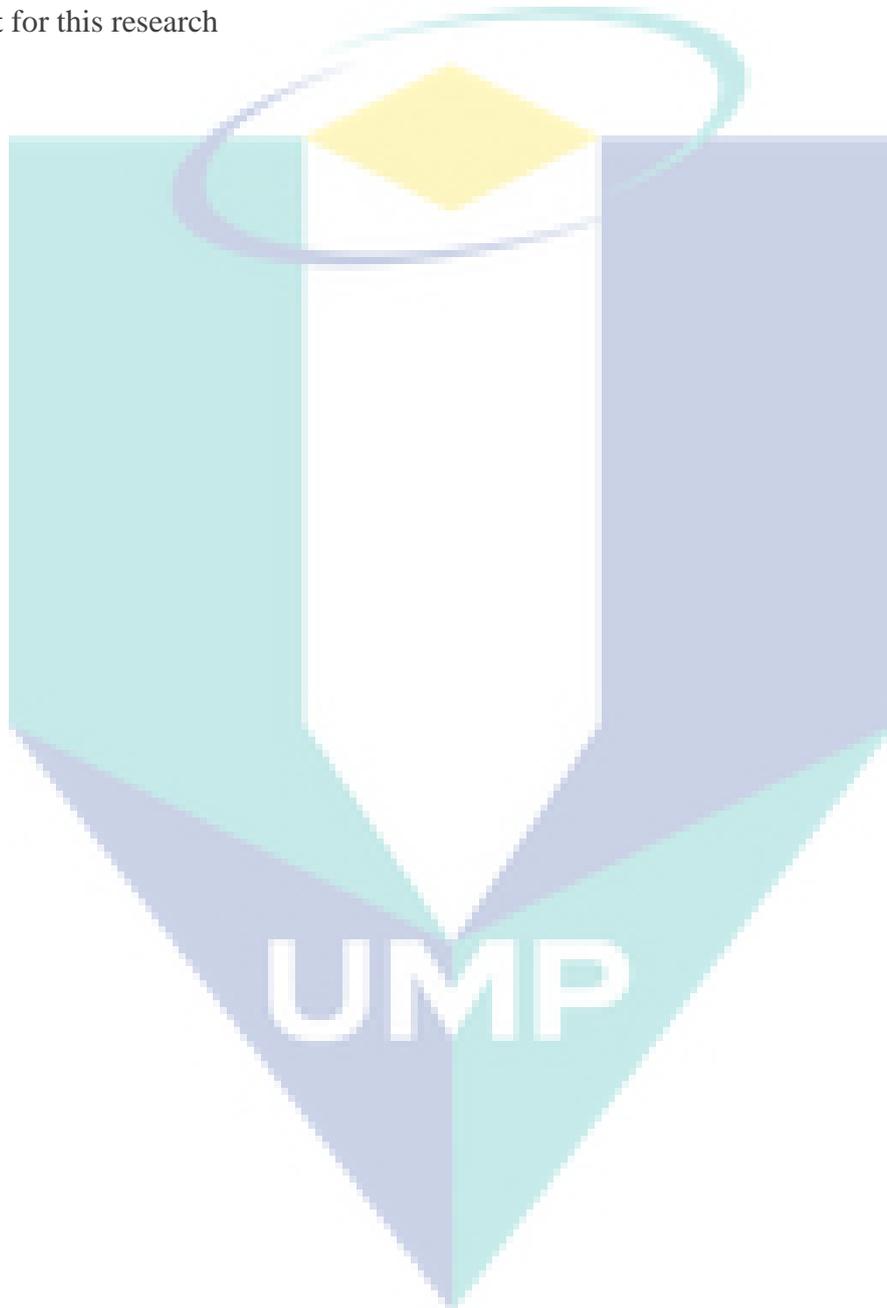
Figure 4. 14: CO<sub>2</sub> adsorption performance with different EDA-AC (2 hours) loading

Table 4.11: Adsorption capacity at breakthrough time for EDA-AC (2 hours) with different loading

Adsorbent Loading	Adsorption loading (g/g)
0.5 g	0.05
1.0 g	0.06
1.5 g	0.09
2.0 g	0.20
3.0 g	0.16

**Error! Reference source not found.** shows the breakthrough curve obtained for EDA-AC (2 hours) adsorption on the prepared activated carbon for 5 different adsorbent weight loading of 0.5, 1.0, 1.5, 2.0 and 3.0 g, at a constant flow rate of 100 mL/min. Increasing the adsorbent loading meaning that the adsorbent bed height to be increased. The breakthrough increased with increasing the bed height. It is known that specific surface area and fixable binding sites for adsorbate is increased with increase in the adsorbent bed height thereby leading to more volume of effluent gas treatment as a result of larger service area provided (Auta, & Hameed 2014). In this research, it was seen that adsorption capacity increased with increasing bed height due to an increase in the surface area of adsorbent, which provided more binding sites for the adsorption (Ahmad, &

Hameed 2010) reported in their work that when the bed height was reduced, axial dispersion phenomena predominated in the mass transfer and reduced the diffusion of the solute, and therefore the solute had not enough time to diffuse into the whole of the adsorbent mass. Beyond the adsorbent loading of 2.0g, the curve shows no appreciable change with further increase in bed height, hence 2.0g has been chosen as optimized bed height for this research



## CHAPTER 5

### CONCLUSION AND RECOMMENDATION

#### 5.1 Conclusion

This study revealed that the modification of the rice husk activated carbon using basic chemicals such as PEI, APTES and EDA could enhance the CO<sub>2</sub> adsorption performance. It was due to the chemisorption process between the N-H group from the chemicals with the surface of activated carbon. The N-H group is a basic site that could generate new sites for CO<sub>2</sub> adsorption. It can be concluded that the increasing of the CO<sub>2</sub> adsorption performance was contributed by chemisorption instead of physisorption. The conclusion was supported by the characterization results whereas the surface morphology and the surface area were changed after loading with the chemicals.

#### 5.2 Recommendation

The experiments of this research were conducted by 3 students undergraduate. Therefore, the parameters used are different and it was difficult to compare the performance of CO<sub>2</sub> adsorption for different samples. Hope that there will be postgraduate student that could extend the study of this research in the future. So that more significant results could be obtained in order to produce the novelty adsorbent to overcome the CO<sub>2</sub> emission problem. Besides, the experimental set up have to be upgraded with sophisticated equipment such as digital flow meter and digital thermometer to obtain the accurate results.

## REFERENCES

- Adinata, D., Wandaud, W. & Aroua, M. 2007. Preparation and characterization of activated carbon from palm shell by chemical activation with  $K_2CO_3$ . *Bioresource Technology*, 98(1), 145–149. doi:10.1016/j.biortech.2005.11.006
- Ahmad, A. A. & Hameed, B. H. 2010. Fixed-bed adsorption of reactive azo dye onto granular activated carbon prepared from waste. *Journal of Hazardous Materials*, 175(1–3), 298–303. doi:10.1016/j.jhazmat.2009.10.003
- Auta, M. & Hameed, B. H. 2014. Adsorption of carbon dioxide by diethanolamine activated alumina beads in a fixed bed. *Chemical Engineering Journal*, 253, 350–355. doi:10.1016/j.cej.2014.05.018
- Boonpoke, A., Chiarakorn, S., Laosiripojana, N., Towprayoon, S. & Chidthaisong, A. 2011. Investigation of  $CO_2$  adsorption by bagasse-based activated carbon. *Korean Journal of Chemical Engineering*, 29(1), 89–94. doi:10.1007/s11814-011-0143-0
- Caglayan, B. S. & Aksoylu, A. E. 2013.  $CO_2$  adsorption on chemically modified activated carbon. *Journal of Hazardous Materials*, 252–253, 19–28. doi:10.1016/j.jhazmat.2013.02.028
- Cheenmatchaya, A. & Kungwankunakorn, S. 2014. Preparation of Activated Carbon Derived from Rice Husk by Simple Carbonization and Chemical Activation for Using as Gasoline Adsorbent. *International Journal of Environmental Science and Development*, 171–175. doi:10.7763/IJESD.2014.V5.472
- Chen, Y., Zhu, Y., Wang, Z., Li, Y., Wang, L., Ding, L., Gao, X. et al. 2011a. Application studies of activated carbon derived from rice husks produced by chemical-thermal process—A review. *Advances in Colloid and Interface Science*, 163(1), 39–52. doi:10.1016/j.cis.2011.01.006
- Chen, Y., Zhu, Y., Wang, Z., Li, Y., Wang, L., Ding, L., Gao, X. et al. 2011b. Application studies of activated carbon derived from rice husks produced by chemical-thermal process—A review. *Advances in Colloid and Interface Science*, 163(1), 39–52. doi:10.1016/j.cis.2011.01.006
- Daifullah, A. A. ., Girgis, B. . & Gad, H. M. . 2004. A study of the factors affecting the removal of humic acid by activated carbon prepared from biomass material. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 235(1–3), 1–10. doi:10.1016/j.colsurfa.2003.12.020

- Dali, A., Ibrahem, A. S., & Hadi, A. 2012. General study about activated carbon for adsorption carbon dioxide. *J Purity Utility React Environ*, 1(5), 206–221.
- Dong, A., Xie, J., Wang, W., Yu, L., Liu, Q. & Yin, Y. 2010. A novel method for amino starch preparation and its adsorption for Cu(II) and Cr(VI). *Journal of Hazardous Materials*, 181(1–3), 448–454. doi:10.1016/j.jhazmat.2010.05.031
- Ghosh, R. 2013. A Review Study on Precipitated Silica and Activated Carbon from Rice Husk. *Journal of Chemical Engineering & Process Technology*, 4(4). doi:10.4172/2157-7048.1000156
- Hamza, U. D., Shawal, N. & Nasri, B. I. N. 2015. CO<sub>2</sub> ADSORPTION ON SUSTAINABLE BIOMASS DERIVED ACTIVATED CARBON: A MINI-REVIEW 2013(October), 1–5.
- Heidari, A., Younesi, H., Rashidi, A. & Ghoreyshi, A. A. 2014. Evaluation of CO<sub>2</sub> adsorption with eucalyptus wood based activated carbon modified by ammonia solution through heat treatment. *Chemical Engineering Journal*, 254, 503–513. doi:10.1016/j.cej.2014.06.004
- Hosseini, S., Eghbali Babadi, F., Masoudi Soltani, S., Aroua, M. K., Babamohammadi, S. & Mousavi Moghadam, A. 2017. Carbon dioxide adsorption on nitrogen-enriched gel beads from calcined eggshell/sodium alginate natural composite. *Process Safety and Environmental Protection*, 109, 387–399. doi:10.1016/j.psep.2017.03.021
- Houshmand, A., Shafeeyan, M. S., Arami-Niya, A. & Daud, W. M. A. W. 2013. Anchoring a halogenated amine on the surface of a microporous activated carbon for carbon dioxide capture. *Journal of the Taiwan Institute of Chemical Engineers*, 44(5), 774–779. doi:10.1016/j.jtice.2013.01.014
- Korobochkin, V. V, Tu, N. V & Hieu, N. M. 2016. Production of activated carbon from rice husk Vietnam. *IOP Conference Series: Earth and Environmental Science*, 43, 12066. doi:10.1088/1755-1315/43/1/012066
- Lee, C. S., Ong, Y. L., Aroua, M. K. & Daud, W. M. A. W. 2013. Impregnation of palm shell-based activated carbon with sterically hindered amines for CO<sub>2</sub> adsorption. *Chemical Engineering Journal*, 219, 558–564. doi:10.1016/j.cej.2012.10.064
- Leung, D. Y. C., Caramanna, G. & Maroto-Valer, M. M. 2014. An overview of current status of carbon dioxide capture and storage technologies. *Renewable and Sustainable Energy Reviews*, 39, 426–443. doi:10.1016/j.rser.2014.07.093
- LI, F., YI, H., TANG, X., NING, P., YU, Q. & KANG, D. 2010. Adsorption of carbon dioxide by coconut activated carbon modified with Cu/Ce. *Journal of Rare Earths*,

28, 334–337. doi:10.1016/S1002-0721(10)60375-4

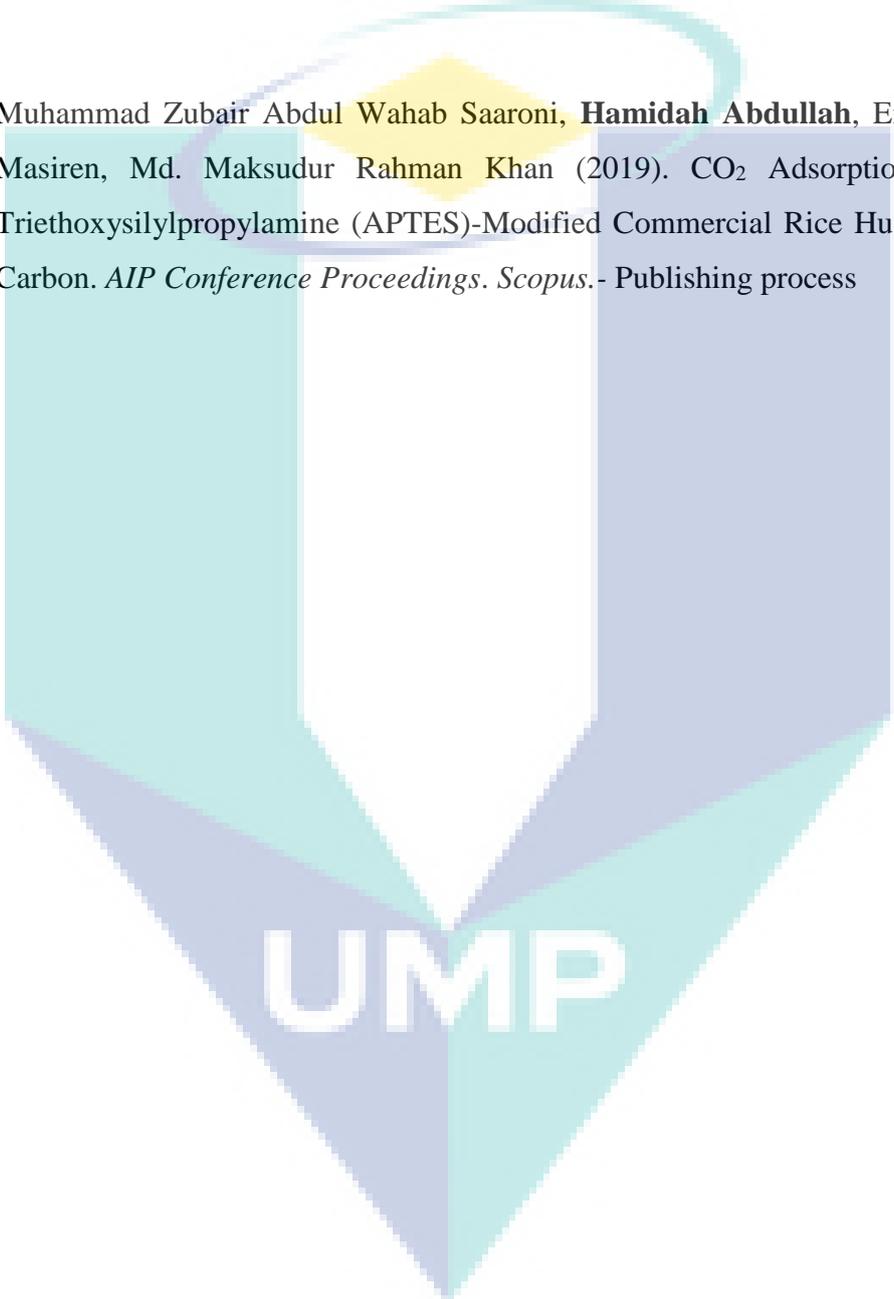
- Li, Z., Chang, X., Zou, X., Zhu, X., Nie, R., Hu, Z. & Li, R. 2009. Chemically-modified activated carbon with ethylenediamine for selective solid-phase extraction and preconcentration of metal ions. *Analytica Chimica Acta*, 632(2), 272–277. doi:10.1016/j.aca.2008.11.001
- Liu, Z., Pudasainee, D., Liu, Q. & Gupta, R. 2015a. Post-combustion CO<sub>2</sub> capture using polyethyleneimine impregnated mesoporous cellular foams. *Separation and Purification Technology*, 156, 259–268. doi:10.1016/j.seppur.2015.10.009
- Liu, Z., Pudasainee, D., Liu, Q. & Gupta, R. 2015b. Post-combustion CO<sub>2</sub> capture using polyethyleneimine impregnated mesoporous cellular foams. *Separation and Purification Technology*, 156, 259–268. doi:10.1016/j.seppur.2015.10.009
- Masoud, M. S., El-Saraf, W. M., Abdel - Halim, A. M., Ali, A. E., Mohamed, E. A. & Hasan, H. M. I. 2016. Rice husk and activated carbon for waste water treatment of El-Mex Bay, Alexandria Coast, Egypt. *Arabian Journal of Chemistry*, 9, S1590–S1596. doi:10.1016/j.arabjc.2012.04.028
- Masoum Raman, S. N., Jamari, S. S., Abdul Samad, N. A. F. & Ismail, N. A. 2016. Investigation of impregnated commercial rice husks activated carbon with alkanolamine as carbon dioxide (CO<sub>2</sub>) adsorbent. *ARPJ Journal of Engineering and Applied Sciences*, 11(4), 2167–2173.
- Mohanta, K. Kumar, D. & Prakash, O. 2012. Properties and Industrial Applications of Rice husk: A review. *International journal of Emerging Technology and Advanced Engineering*, 2(10), 86–90.
- Plaza, M. G., Pevida, C., Arenillas, A., Rubiera, F. & Pis, J. J. 2007. CO<sub>2</sub> capture by adsorption with nitrogen enriched carbons. *Fuel*, 86(14 SPEC. ISS.), 2204–2212. doi:10.1016/j.fuel.2007.06.001
- Przepiórski, J., Skrodzewicz, M. & Morawski, A. . 2004. High temperature ammonia treatment of activated carbon for enhancement of CO<sub>2</sub> adsorption. *Applied Surface Science*, 225(1–4), 235–242. doi:10.1016/j.apsusc.2003.10.006
- Rashidi, A. N., Yusup, S. & Hon, L. 2013. Kinetic Studies on Carbon Dioxide Capture using Activated Carbon. *Chemical Engineering Transactions*, 35, 361–366. doi:10.3303/CET1335060
- Shafeeyan, M. S., Daud, W. M. A. W., Houshmand, A. & Shamiri, A. 2010. A review on surface modification of activated carbon for carbon dioxide adsorption. *Journal of Analytical and Applied Pyrolysis*, 89(2), 143–151. doi:10.1016/j.jaap.2010.07.006

- Shin, G.-J., Rhee, K. & Park, S.-J. 2016. Improvement of CO<sub>2</sub> capture by graphite oxide in presence of polyethylenimine. *International Journal of Hydrogen Energy*, 41(32), 14351–14359. doi:10.1016/j.ijhydene.2016.05.162
- Shin, G. J., Rhee, K. Y. & Park, S. J. 2016. Improvement of CO<sub>2</sub> capture by graphite oxide in presence of polyethylenimine. *International Journal of Hydrogen Energy*, 41(32), 14351–14359. doi:10.1016/j.ijhydene.2016.05.162
- Shin, G. J., Rhee, K. Y. & Park, S. J. 2016. Improvement of CO<sub>2</sub> capture by graphite oxide in presence of polyethylenimine. *International Journal of Hydrogen Energy*, 41(32), 14351–14359. doi:10.1016/j.ijhydene.2016.05.162
- Singh, V. K. & Anil Kumar, E. 2016. Measurement and analysis of adsorption isotherms of CO<sub>2</sub> on activated carbon. *Applied Thermal Engineering*, 97, 77–86. doi:10.1016/j.applthermaleng.2015.10.052
- Somy, A., Mehrnia, M. R., Amrei, H. D., Ghanizadeh, A. & Safari, M. 2009. Adsorption of carbon dioxide using impregnated activated carbon promoted by Zinc. *International Journal of Greenhouse Gas Control*, 3(3), 249–254. doi:10.1016/j.ijggc.2008.10.003
- Spigarelli, B. P. & Kawatra, S. K. 2013. Opportunities and challenges in carbon dioxide capture. *Journal of CO<sub>2</sub> Utilization*, 1, 69–87. doi:10.1016/j.jcou.2013.03.002
- Tan, I. A. W., Ahmad, A. L. & Hameed, B. H. 2008. Adsorption of basic dye using activated carbon prepared from oil palm shell : batch and fixed bed studies 225, 13–28. doi:10.1016/j.desal.2007.07.005
- Tan, Y. L., Islam, M. A., Asif, M. & Hameed, B. H. 2014. Adsorption of carbon dioxide by sodium hydroxide-modified granular coconut shell activated carbon in a fixed bed. *Energy*, 77, 926–931. doi:10.1016/j.energy.2014.09.079
- Uçar, S., Erdem, M., Tay, T. & Karagöz, S. 2009. Preparation and characterization of activated carbon produced from pomegranate seeds by ZnCl<sub>2</sub> activation. *Applied Surface Science*, 255(21), 8890–8896. doi:10.1016/j.apsusc.2009.06.080
- Wang, J., Chen, H., Zhou, H., Liu, X., Qiao, W., Long, D. & Ling, L. 2013. Carbon dioxide capture using polyethylenimine-loaded mesoporous carbons. *Journal of Environmental Sciences*, 25(1), 124–132. doi:10.1016/S1001-0742(12)60011-4
- Yadavalli, G., Lei, H., Wei, Y., Zhu, L., Zhang, X., Liu, Y. & Yan, D. 2017. Carbon dioxide capture using ammonium sulfate surface modified activated biomass carbon. *Biomass and Bioenergy*, 98, 53–60. doi:10.1016/j.biombioe.2017.01.015
- Yang, H., Xu, Z., Fan, M., Gupta, R., Slimane, R. B., Bland, A. E. & Wright, I. 2008.

- Progress in carbon dioxide separation and capture: A review. *Journal of Environmental Sciences*, 20(1), 14–27. doi:10.1016/S1001-0742(08)60002-9
- Yin, C. Y., Aroua, M. K. & Daud, W. M. A. W. 2007. Impregnation of palm shell activated carbon with polyethyleneimine and its effects on Cd<sup>2+</sup> adsorption. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 307(1–3), 128–136. doi:10.1016/j.colsurfa.2007.05.012
- Yin, C. Y., Aroua, M. K. & Daud, W. M. A. W. 2008. Polyethyleneimine impregnation on activated carbon: Effects of impregnation amount and molecular number on textural characteristics and metal adsorption capacities. *Materials Chemistry and Physics*, 112(2), 417–422. doi:10.1016/j.matchemphys.2008.05.075
- Yong, Z., Mata, V. G. & Rodrigues, A. E. 2001. Adsorption of CO<sub>2</sub> on Chemically Modified High Surface Area Carbon-based Adsorbents at high Temperatures. *Adsorption*, 7(1), 41–50. doi:10.1023/A:1011220900415
- Zhang, Y., Zheng, R., Zhao, J., Ma, F., Zhang, Y. & Meng, Q. 2014. Characterization of H<sub>3</sub>PO<sub>4</sub>-Treated Rice Husk Adsorbent and Adsorption of Copper (II) from Aqueous Solution. *Biomedical Research International*, 3(2), 1–9.
- Zhu, J., Yang, J. & Deng, B. 2009. Enhanced mercury ion adsorption by amine-modified activated carbon. *Journal of Hazardous Materials*, 166(2–3), 866–872. doi:10.1016/j.jhazmat.2008.11.095
- Zulkurnai, N. Z., Md. Ali, U. F., Ibrahim, N. & Abdul Manan, N. S. 2017. Carbon Dioxide (CO<sub>2</sub>) Adsorption by Activated Carbon Functionalized with Deep Eutectic Solvent (DES). *IOP Conference Series: Materials Science and Engineering*, 206, 12001. doi:10.1088/1757-899X/206/1/012001

## LIST OF PUBLICATION

1. **Hamidah Abdullah**, Md Maksudur Rahman Khan, Huei Ruey Ong, Zahira Yaakob (2017). Modified TiO<sub>2</sub> photocatalyst for CO<sub>2</sub> photocatalytic reduction: An overview. *Journal of CO2 Utilization* 22, 15-32. *Q1*.
2. Muhammad Zubair Abdul Wahab Saaroni, **Hamidah Abdullah**, Emyra Ezzaty Masiren, Md. Maksudur Rahman Khan (2019). CO<sub>2</sub> Adsorption Using 3-Triethoxysilylpropylamine (APTES)-Modified Commercial Rice Husk Activated Carbon. *AIP Conference Proceedings. Scopus*. - Publishing process



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