Synthesis of metakaolin alkali based geopolymer for Hydrogen adsorption study

by

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16862

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

MAY 2015

Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by

(ASSOC. PROF DR. SURIATI BINTI SUFIAN**)**

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
MAY 2015

CERTIFICATION OF ORIGINALITY

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

(SHANMUGAM A/L GUNASEKARAN)

ABSTRACT

Hydrogen is not only an energy carrier but it's also one of the substituting source that can be replace fossil fuels. Therefore possible adsorbent extensively being tested for better hydrogen adsorption. Recently, there are researches on hydrogen storage by using developed materials such as complex hydride, carbon nanotubes, zeolites and alloy metal. Geopolymer is proposed as a potential adsorbent due to economically and environmental friendly properties and lower cost compared to other developed materials and also derived from industrial waste. Thus, the scope of the hydrogen storage is wide, the author has narrowed down his study on hydrogen adsorption by using synthesized metakaolin alkali based geopolymer. Different molarity of alkali activator of sodium hydroxide (NaOH) of 8M, 10M and 12M were used to synthesis raw material of metakaolin in order to find which one is the best parameter for hydrogen adsorption uptake. Result shown that hydrogen adsorption on least molarity of alkali activator (8M), it adsorbs about 1.34 weight percentage though slightly lower than alkali activator of 12M which has about 1.49 weight percent. In nutshell, as molarity of the alkali activator (NaOH) increases, the hydrogen adsorption (wt%) also increases.

ACKNOWLEDGEMENT

In completion of this final year project, I would like to thank Universiti Teknologi PETRONAS for providing me with the opportunity to conduct this study for my final year project. I would also like to express my gratitude to my supervisor, Assoc.Pro Dr Suriati binti Sufian fo her unconditional guide and support throughout the project. I am also grateful to Dr Abdus Salam for the knowledge he shared with me on conducting experiment related to this project area. Not forgetting, special thanks to lab technicians and past final year project student Siti Jarodah and some postgraduate students for their co-operation that helped me to conduct my experiment smoothly. Finally, I would like to thank my fellow coursemates for their continuous support and encouragement which driven me to complete this project successfully.

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ABBREVIATION AND NOMENCLATURES

H_2	Hydrogen gas
CO_2	Carbon dioxide gas
DOE	Department of energy
BET	Brunauer Emmette Teller
FESEM	Field emitted Scanning Electron Microscopy
XRD	X-Ray Diffraction
Wt%	Weight percentage
Al_2O_3	Metakaolin
SiO2	Silica Oxide

CHAPTER 1

INTRODUCTION

1.1 Background of study

1.1.1 Hydrogen as a future fuel

Hydrogen is one of the promising alternative energy storage that will replace fossil fuels because it is a source of clean and efficient energy. Other than, hydrogen being used primarily in other processes such as ammonia manufacturing and synthesis of methanol. Currently, several researches had been carried out in order to develop material such as complex hydride, carbon nanotubes, zeolites and alloys metal for hydrogen storage in large quantities. Based on NASA's space program, hydrogen can be used to fuel the vehicles and also provide power for homes and offices. Hydrogen being produced from hydrocarbons by applying heat and extracted from natural gas. There are a few methods of producing hydrogen is environmentally beneficial. Hydrogen fuel is an emission-free fuel that utilizes electrochemical cells in order to power the vehicles and also electric devices.

Extensive researches are being carried out to capture and store the hydrogen. There are plenty of advantages compared to fossil fuels. For example, there will be no pollution caused by using hydrogen as a fuel and the by product will be only water. It also needed lower temperature to operate the vehicle and it is more efficient than diesel and other gas engines. Other than that, hydrogen fuel is quieter than diesel and gas engines. Therefore, the hydrogen as a future fuel which is replacing fossil fuels are being supported and chased very rapidly. Based on U.S Department of energy, the automakers are attempting a method is able to mass produce vehicles that is fuel by hydrogen.

1.1.2 Hydrogen storage challenges

There are a lot of major challenges for hydrogen production and storage. Hydrogen storage is not only fuel source but it also used for energy storage. Based on many researches have been done so far, for the transportation there are few technical challenges for hydrogen storage within few constraints. Weight and volume of hydrogen storage are generally higher than the petroleum fueled vehicles. Other challenges for hydrogen storage is efficiency. This is because the energy requirement for the hydrogen inlet and outlet is really matters for the reversible solid state materials.

Besides that, durability also being one of the hydrogen storage challenges which is needed material and components to store hydrogen systems within 1500 cycles of lifetime. The refueling time are too long in order to develop the hydrogen storage systems to be in short. The other challenges for hydrogen storage is cost. The hydrogen system is very expensive compared to other conventional petroleum fuels system and to overcome this challenge, low cost materials and components are needed for the hydrogen storage. Lastly, the life cycle and efficiency analysis are lack for hydrogen storage systems.

1.1.3 Hydrogen storage methods

There are different forms such as compressed gas and cryogenic liquid used for hydrogen storage. Hydrogen storage can be done using six different methods such as high pressure gas cylinders, liquid hydrogen in cryogenic tanks, adsorption of hydrogen on materials, absorption of hydrogen in a metal, covalent and ionic compounds that bonded chemically and lastly through oxidation of reactive metals with water. Thus the hydrogen storage method is too wide for storing the energy therefore, the author have been narrowed down the hydrogen storage method into one of the method which is adsorption of the hydrogen on materials.

The concept hydrogen adsorption can be stored on to the metal surfaces, where it attached hydrogen to the surface of the solid metals by as a hydrogen molecules (H_2) or by hydrogen atom (H). Thus, the hydrogen can be strongly bound within molecular structure with lower density compared to other methods such as hydrogen absorption, metallic hydride and complex hydride.

1.2 Problem statement

There are a lot of major challenges for hydrogen production and storage. Due to major challenges, there are extensive researches are carried out in order to find various methods that can adsorb hydrogen efficiently and effectively. Until now, there is no significant research have met DOE target of Hydrogen storage that is 6 wt%. The hydrogen adsorption methods that been widely used are hydrogen adsorption on zeolites, reactive metals such as Li, Ni, Mg and etc, porous and nonporous materials and nanostructures materials. Therefore, the searching of best hydrogen adsorbent on material are still in the process of research and also best parameter for synthesized metakaolin with alkali activator for better hydrogen adsorption study.

1.3 Objective

The main objectives of the study are:

- To synthesize and characterize the metakaolin alkali based geopolymer by using Analytical techniques.
- To test the hydrogen adsorption with the synthesized geopolymer by using the fixed bed reactor
- To find the best parameter for alkali activator in order to synthesis metakaolin for maximum hydrogen uptake.

1.4 Scope of study

This research work scope focused on the use of metakaolin alkali based geopolymers as hydrogen adsorbent. Different samples of metakaolin alkali based geopolymer synthesized by using different solid-liquid ratio with sodium hydroxide (NaOH). The samples are mixed at ambient temperature under specific ratio before the slurry mixture is place into the oven at 60°C for 24 hours. Characterization of the geopolymer done by using Brunauer Emmette Teller (BET), Field Emitted Scanning Electron Microscopy (FESEM) and X-Ray Diffraction (XRD). Lastly, the hydrogen adsorption capabilities of synthesized metakaolin alkali based geopolymers tested using fixed bed reactor.

CHAPTER 2

LITERATURE REVIEW

The literature review is mainly explaining basic theory of adsorption, type of methods that been used to adsorb hydrogen and geopolymer properties. In addition, previous work on hydrogen adsorption properties are discussed and adjusted in this section.

2.1 Theory of adsorption

Based on adsorption theory from internet, adsorption is a separation process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid adsorbent. Compared with absorption, where a substance diffuses into a liquid or solid to form a solution. The term sorption is comprised with both processes, while desorption is known as reverse process. When the adsorbent become saturated with the adsorbate, the adsorbent will be generated by acid wash or water-wash. The mechanism of adsorption process can be explained in three steps which are diffusion, migration and adsorption process (Refer FIGURE 2.1).

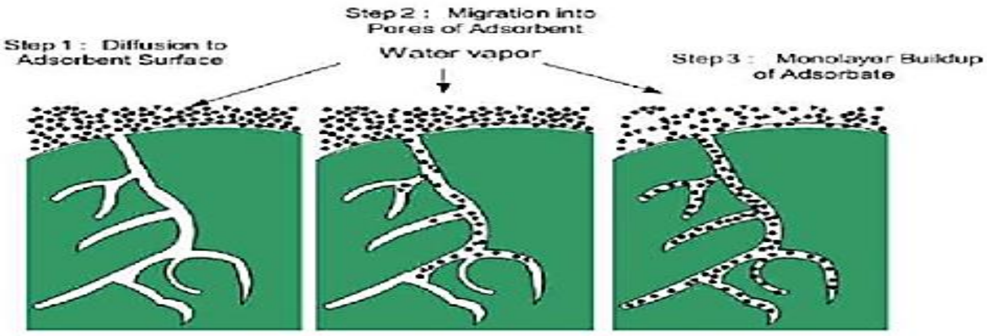


FIGURE 2.1. Mechanism of Adsorption (KIM, Chea, & Kim, 2012)

According to (KIM *et al*., 2012), in the mechanism of adsorption, first, the molecule diffusion process into the thin layer of the fluid or known as fluid film which is attached on the adsorbent. According to developing of diffusion, the second phase is the process which attached the vapor or gas along the pores. It is called as mixed diffusion because it consists of two diffusions which are pore diffusion and surface diffusion. The last process is the adsorption process in the pore adsorption site.

2.2 Type of adsorption

There are two types of adsorption which is physical adsorption (physisorption) which is also known as Vander Waal's adsorption. This type of adsorption is a reversible by decreasing its pressure and also by heating. Other type of adsorption is chemical adsorption that is known as chemisorption (Langmuir adsorption), unlike as physisorption this type of adsorption cannot be reversed due to its stronger force of attraction. There are main four factors that had been affecting adsorption which are nature of the adsorbent used, the surface area of the adsorbent, activation of the adsorbent and also experimental conditions such as temperature and pressure.

2.3 Hydrogen storage methods and geopolymer as a potential adsorbent.

2.3.1 Adsorption using geopolymer

Geopolymer adsorbents are scientific interests in recent years due to the two major advantages; low energy consumption and no CO_2 emission in the preparation process. According to M. Wang et,al at present, there are mainly three kinds of aluminosilicate sources for the preparation of geopolymer which are metakaolin (calcined kaolin), fly ash and chemically synthesize kaolin. Though there are different types of modified materials being used as adsorbent for wastewater treatment application, there are still improvements that can be done, which then lead to motivating research and discovery of new adsorbent materials.

Unfortunately, the very change of structure that gives chitosan adsorbing capabilities also makes it easily soluble in weak, dilute acidic solutions. There is another type of geopolymers, the phosphoric acid-based geopolymer, which has been successfully synthesized and characterized by (Le-Ping, XueMin, Shu-Heng, Jun-Li, & Lin, 2010). The authors also have explained that porous structure that presents in geopolymer is one of the reasons fot better adsorption compared to other adsorbents.

Based on the researches on hydrogen adsorption as an energy carrier, there are reliable researches that has been carried out to find the best method in order to adsorb hydrogen. Refering to research paper on materials for hydrogen storage by Andreas Zuttel (2003), there are six main methods of hydrogen storage, Zuttel had explained hydrogen storage is in gas phase. Besides that, for the physical adsorption of hydrogen required substrate that consists of materials that have a higher specific surface area like activated or nanostructure carbons.

Based on the research from California institute of Technology (N.D), hydrogen has a single electron in the atom where it can react with other metals form covalent molecules such as H_2. Physisorption is known as physical adsorption has been carried out in this research as an attractive storage method. The adsorption of the hydrogen is fast and fully reversible where is does not require bulk solid diffusion or chemical dissociation. By referring to research paper by Salam,M.A, Sufian,S and Ye Lwin(2014), on hydrogen adsorption capacity investigation of Ni-Co-Al mixed oxides using the density functional theory, using reversible hydrogen storage system in order to adsorb hydrogen by physisorption and chemisorption and the hydrogen is generally stored in a molecular forms. The conditions to adsorb hydrogen effectively where it needs high pressure and temperature.

Based on K.Mark Thomas (2007), the amount of hydrogen adsorbed on porous material is directly related to temperature and pressure. The hydrogen physisorption on porous materials required stronger temperature in order to store hydrogen by increasing the storage capacity requirement. He stated that the amount of hydrogen adsorbed is normally can differentiate with other method by adsorption isotherms dependent with temperature and pressure. For fast hydrogen charging and discharging characteristics, the adsorption/desorption is required for the hydrogen adsorption on the porous materials.Based on hydrogen adsorption properties of nano and microstructures of ZnO by Rizwan Wahab *etc al* (2013), the hydrogen storage properties in materials are normally applied in automotive industries .This is because its properties such as high gravimetric, high volumetric density , fast kinetics, low cost, low temperature dissociation properties and also longer time stability. The nanostructured materials also can simply affect the adsorption properties on the surface by disturbing the thermodynamics

There are studies on synthesis geo-polymer as a potential adsorbent widely discussed by the researchers. T.W. Cheng a, M.L. Lee a, M.S. Ko a, T.H. Ueng a, S.F. Yang (2011) on the heavy metal adsorption characteristics on metakaolin-based geopolymer. The heavy metal adsorption characteristics on metakaolin-based geopolymer research paper, stated that a higher pH value can maximize the adsorption of the heavy metal ion on the geopolymer. The reaction that involved in adsorption on geopolymer is normally an endothermic reaction. The metakaolin besed geopolymer with alkaline solution normally has a potential adsorption property where the heavy metal ions acts as a single molecular layer for the adsorption on geopolymer.

According to Barbara Panella (2006), there are three main experimental techniques are used to study the physical adsorption (physisorption) on porous materials. Based on result by the author, larger specific surface area is required for higher hydrogen adsorption capacity and to increase the interaction energy. Physisorption is a potential hydrogen adsorbent due to its complete reversibility and fast kinetics. Besides that, to release hydrogen for the adsorption, only very small amount of energy is needed.

2.4 Background of Geopolymer

The term geopolymer was first invented by J. Davidovits in the late 1970s and now identifies as a family of amorphous alkali or alkali-silicate activayed aluminosilicate binders (Colangelo, Roviello, Ricciotti, Ferone, & Cioffi, 2013). Geopolymers are material which is made up of polymeric Si-O-Al functional group, creating a framework similar to zeolites, but more amorphous instead of crystalline. There are small aluminosilicate clusters with dispersed pores within a highly porous network (Huang & Han, 2011). Since the late seventies of the 20th century, geopolymers have been considered for replacing traditional structural materials by reason of their excellent properties and high performance (Davidovits, 1982).

Geopolymers have been used in many applications and one of the major applications is in the construction industry. This is due to its quick curing time and high tensile strength. Other applications of the geopolymers include archaeology and heavy metal adsorption. Geopolymer can be synthesized easily under normal ambient condition using different raw materials, for instance metakaolin and fly ash. Metakaolin is simply a heated kaolin which also known as china clay while fly ashes are waste from thermal power factories. Both raw materials have high aluminosilicate and highly favourable to synthesize geopolymers.

2.5 Geopolymerization

Geopolymerization is a geo-synthesis reaction involving silico-aluminitae sources. Source of alumina and silica acts as a source of precursor that generally dissolved into any alkaline solution, and also synthesized by alkaline and/or silicate activation which lends itself to the process of geopolymerization (Peter Duxson *et al*., 2007; Heah et al., 2012).

According to (Xu & Van Deventer, 2002), the basic step of geopolymerization is the dissolution of the solid alumina silicate oxide in a KOH or NaOH solution to form SiO_4 and AlO_4 tetrahedral units. It is newly developing field of research which provides a mature and cost effective 32 solution to many problems by utilizing solid wastes or byproducts where hazardous residue has to be stored under critical environmental conditions such as high temperature, low temperature, high pressure and low pressure based on research paper from Khale and Chaudhary (2007).

2.6 Metakaolin raw material

Main sources of metakaolin are either kaolin or paper sludge after suitable treatment. Kaolin is one of the most widely used industrial minerals where its world's total output exceeds 25 million tonnes (Nkoumbou *et al*., 2009). Under normal environmental conditions, kaolin is quite stable. However, when kaolin heated to temperature of 650 - 900 C, it loses 14% of its mass in bound hydroxylions (Rashad, 2013b). This heat treatment, or calcination, breaks down the structure of kaolin such that the alumina and silica layers become puckered and lose their long-range order.

Resulting from this dehyroxylation and disorder is metakaolin, a highly reactive transition phase (Barnes & Bensted, 2002), amorphous material with pozzolanic and latent hydraulic reactivity, generally can be used in applications that involved in cement (Kostuch, Walters, & Jones, 2000). Metakaolin is essentially an anhydrous aluminisilicate that is produced by the thermal composition of (Duxson, Mallicoat, Lukey, Kriven, & Van Deventer, 2007), a naturally occurring clay containing kaolinite, $Al_2Si_2O_5(OH_4)$ and trace amounts of silica and other minerals.

The hydroxyl ions are strongly bonded to the Alumini-silicate framework structure, thus only temperature in excess of 550^{o}C can be eliminate the framework structure. When the large-layer structured materials that consists of kaolinite are subjected to intensive thermal treatment (850^{o}C), the material undergoes series of transformation that subsequently reactivity according to given chemical agents. At approximately 600^{o}C, kaolinite loses most of its crystallinity property. This explains that the hexagonal layer structure in kaolinite is partially destroyed at this temperature. Therefore, the original mineral structure becomes disintegrated and forming a material referred to as metakaolin. Thus, metakaolin is a partially ordered structure that cannot rehydrate in the presence of water.

2.7 Alkali Activators

Alkali activators can be divided into two groups which are alkali hydroxide which is meant for dissolution of raw materials that generally specified by sodium and also potassium silicate solution which is acting as a binder (Phair, Van Deventer, & Smith, 2004). As reported in the studies by Khale & Chaudhary, 2007, strong alkalis are required to activate the silicon and aluminium present raw material. Alkali metal salts and/or hydroxide are necessary for the dissolution of silica and alumina as well as for the catalyst of the condensation reaction.

The common activators are NaOH, Na_2SO_4, Na_2CO_3, K_2SO_4, KOH or a little amount of cement clinker. Sodium silicate has been used for more than a century for the production of commercial products such as catalyst, molded articles, special cements and also coatings. Based on Geopolymer and alkali activator by John L.Previs, the soluble silicate is mixed with solid raw materials or other source of multivalent metal ions that promotes the gelation and precipitation of silicates. The more the NaOH get in contact with the reactive solid materials, the more silicate and aluminate monomers are released.

2.8 Synthesis and Characterize Phosphorous Acid-based Geopolymer

2.8.1 Synthesis of sodium hydroxide alkali-based Geopolymer

The synthesis method of alkali based geopolymer according to (LePing *et al.*, 2010), can be done by adding sodium hydroxide to the mixture of metakaolin and α-Al2O3 at ambient temperature. Metal powder such as Al and Fe can be added as a pore-forming agent. This work done have shown that the geopolymers formed will possess different properties as the component ratios are altered. For instance, the amount of pore-forming agent has an effect on the porosity and compressive strength of the synthesized geopolymer. The higher the Al content, the higher the porosity of the sample and the lower the compressive strength. It is also reported that the lower water content will result in higher viscosity and smaller final pore size. However, if the water content is too high, the viscosity will be quite low and lead to the disappearance of all pores.

2.8.2 Characterization and analytical techniques

There are various analytical techniques will be adopted in this studies. Several tests and analysis will be carried out on geopolymer to determine the chemical compositions, surface structure, porosity and particle size using various tools. Besides that, fixed bed reactor will be used for hydrogen adsorption testing.

2.8.2.1 Determination of Pore Size Distribution and Porosity

Brunauer-emmet-Teller (BET) analysis provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a surface area analyser. The technique encompasses external area and pore area evaluations to determine the total specific surface area in cm^2/g yielding important information in studying the effects of surface porosity and particle size in many application. The specific surface area of a powder is generally identified from physical adsorption of a gas on the surface of the solid and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. Physical adsorption can be results from relatively weak forces (Van der Waals forces) between the adsorbate gas molecules and the adsorbent surface area of the test powder.

2.8.2.2 Analysis of Surface morphology

The surface structure of phosphoric acid-based geopolymer is determined using Scanning Electron Microscopy (SEM). Generally SEM occupy high-energy electrons in focused beam of high-energy electrons in order to send a variety of signals at the solid specimen's surface. Therefore, the signals that generally obtained from electron-sample interactions that gives information about the sample about crystalline structure, chemical composition, external morphology (texture), and also orientation of materials that made up the sample. In most applications, data are collected over a selected area of the surface of the sample, and also a 2-dimensional image is generated that display spatial variations in these properties. Figure 2.2 shows an example SEM generated image of a solid sample that explains the surface morphology according to different temperatures as shown below.

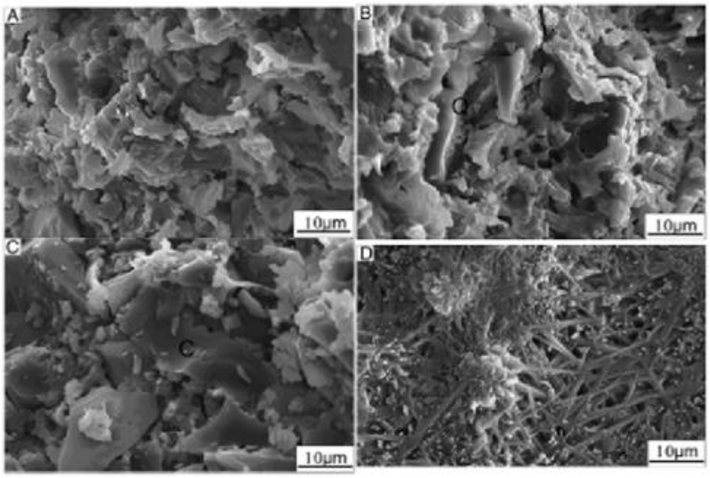


FIGURE 2.2. SEM micrographs of geopolymer heated for 1 h at various temperature: (A) 150^oC, (B) 1050^oC, (C) 1450^oC, and (D) 1550^oC (Liu, Cui, He, Liu, & Gong, 2012

2.8.2.3 X-Ray Diffraction

X-ray Diffraction (XRD) technique is used for a wide variety of material characterization studies. Primarily, the technique getting the information regarding crystalline species in material. Other than for identification of compound, XRD can also be used to grain size of crystalline materials crystallographic structure, determine strain and also preferred orientation. When x-ray diffraction is used in a glancing angle mode, as a function of depth can be obtained by crystalline structure.

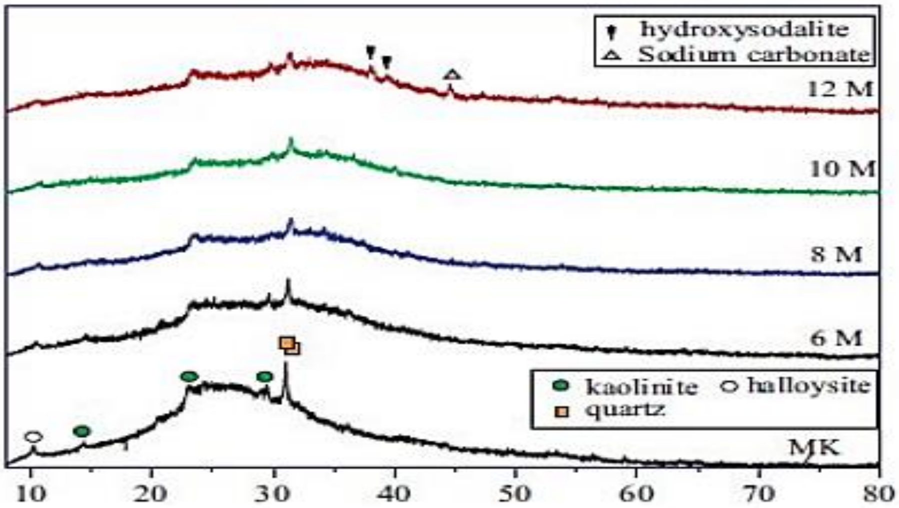


FIGURE 2.3. Co Kα radiation XRD patterns of MK and its geopolymerization products after activation with NaOH solution of 6-12 mol/L at 30^{o}C for 72 h (Zhang *et al.*, 2012).

Figure 2.3 shows the XRD data for metakaolin and the geopolymer samples obtained after 72 h of reaction at 30^{o}C. The metakaolin used is largely amorphous, with a small quantity of quartz as an impurity phase, and minor kaolinite and halloysite. As reported by (Zhang *et al.*, 2012), the broad peak observed from 15 to 35^{o} 2θ metakaolin has been broadened up to 40^{o} 2θ after reaction with NaOH solution, with the center gravity shifted to higher angle, as is well known to occur during geopolymer formation of metakaolin.

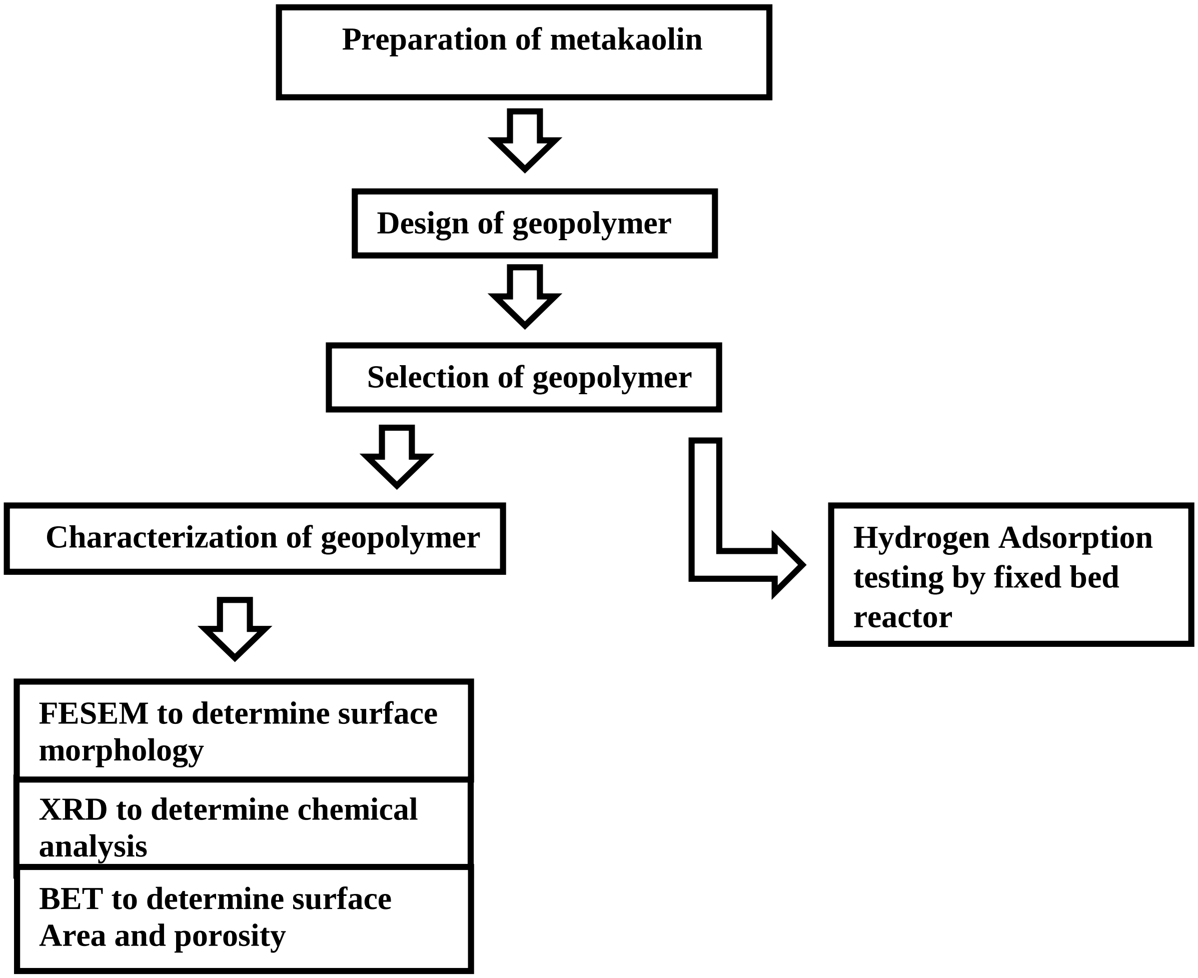
CHAPTER 3

METHODOLOGY

3.1 Procedure

The research work of this study is divided into two main part which are preparation of geopolymer and methods on adsorption of hydrogen gas as an energy source.

1) PREPARATION OF GEOPOLYMER :



i) Preparation and characterization of raw material :

The raw material kaolin will be calcined in the furnace for 750^{o}C for 5 hours to form metakaolin before the material will be used to synthesize phosphoric acid-based geopolymer (Refer TABLE 3.1).

Raw Material	Description
Metakaolin	• Used as Al_2O_3 source for the synthesis of geopolymers • Metakaolin will be produced by the calcinations process of the kaolinite at temperature of 750^{o}C for 5 hours in the furnace • The high temperature metakaolin will be cooled at room temperature for 24 hours.

TABLE 3.1. Preparation of raw material

ii) Synthesis of metakaolin alkali based geopolymer

In this research, phosphoric acid-based geopolymer is synthesized by adopting a method from (Le-Ping *et al*., 2010). Meanwhile, the experimental parameters are adopted from a research by (Hameed, 2009). Geopolymers characteristics are synthesized with different molarity of Sodium hydroxide (NaOH) are used.

Different molarity of Sodium hydroxide (NaOH) which are (8M, 10M, 12 M) are used with different solid-liquid ratio (1-1, 1-2, 2-1 and 3-1). For instance, 5g of metakaolin was used and mixed with 5g of Sodium hydroxide solution. This experimental procedures were repeated with different solid liquid ratio in order to see which is the best option for the synthesizing the metakaolin geopolymers. Moreover, the mixture will be stirred for 1 minute before poured into cubic moulds, and then sealed to prevent water loss. The cubes were cured at 60^{o}C for 24 hours. The dried materials were crushed and sieved to desired mesh size (125-250 µm). The prepared samples were stored in an airtight container for further use.

2) Hydrogen Adsorption testing experiment

There are various researches on hydrogen adsorption using feed bed reactor. Therefore, previous sample research work was used as a guidance from (Salam,Sufian,Lwin & Muregesan, 2013) , The procedure of the hydrogen adsorption using TPPCNF experiment is shown as below :

- Firstly the system was calibrated without the samples into the bed. Then followed by purified nitrogen being sent to remove any remaining gas in the feed reactor bed. The bed kept until it reaches room temperature. Later on the required amount of hydrogen gas and nitrogen gas were sent to fixed bed to conduct H_2 adsorption on the synthesized metakaolin alkali based geopolymer. Lastly, the data acquisition of the gas concentration was measured via RS232 converter.

- The experimental setup is shown below for the hydrogen capacity measurement.

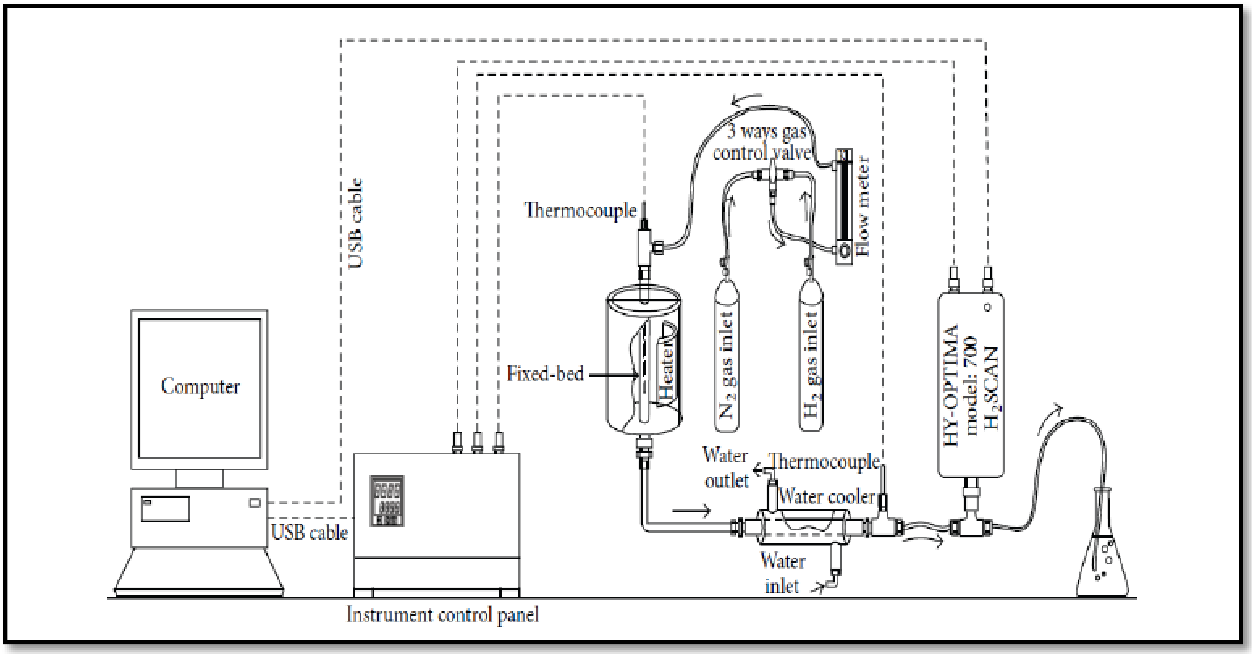


FIGURE 3.1. Diagram of Full Fixed Bed Setup (Salam *et. al*, 2013)

3.2 Gantt chart

No	Detail / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	Project work continues	🟪	🟪	🟪	🟪	🟪	🟪	🟪									
2	Submission of Progress report							●									
										🟪	🟪	🟪	🟪				
3	Project work continues																
4	Pre-SEDEX											●					
5	Submission of Draft Dissertation												●				
6	Submission of Dissertation (Soft bound)													●			
7	Submission of Technical paper													●			
8	Viva presentation															●	
9	Submission of Project Dissertation (Hard bound)																●

TABLE 3.2. Gantt chart

● Suggested Milestone

🟪 Process

3.3 Key milestone

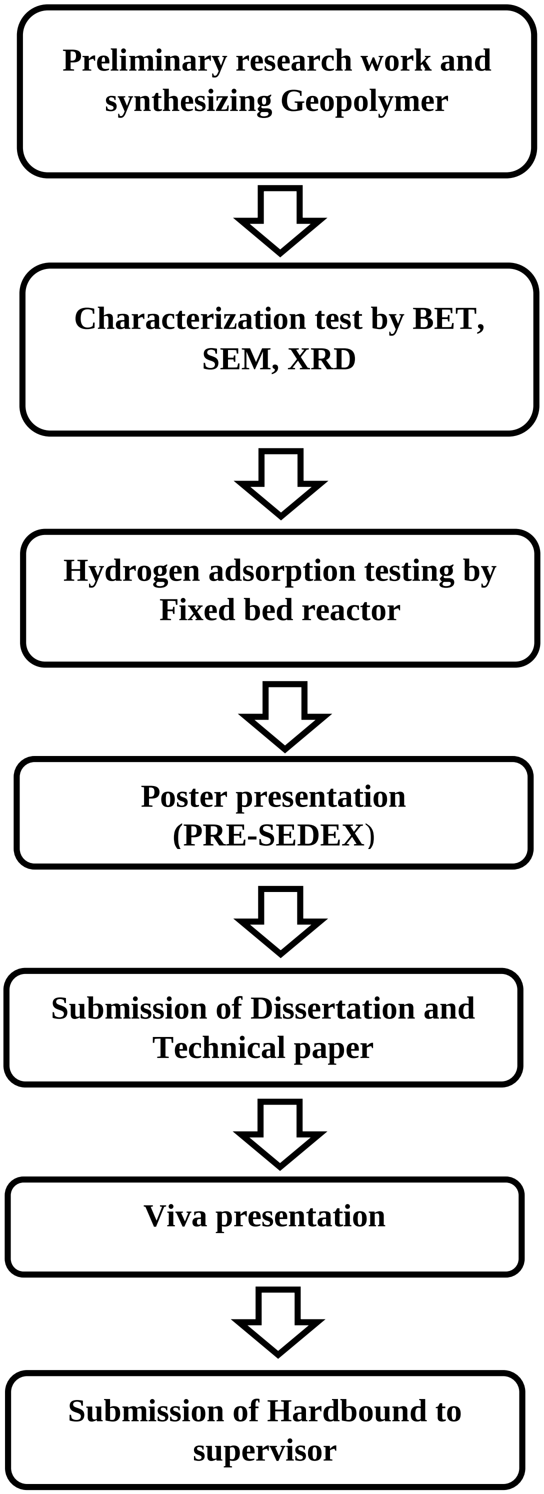


FIGURE 3.2. Key Milestone

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Synthesis of Metakaolin acid based geopolymer

The synthesis method of phosphoric acid-based geopolymer according to (LePing *et al*., 2010), can be done by adding to the sodium hydroxide with metakaolin (Al_2O_3) at ambient temperature. Before proceed with the synthesis process, Kaolin was calcined at 750°C in furnace for 6 hours. Geopolymers characteristics are synthesized with different molarity of Sodium hydroxide (NaOH) are used. Different molarity of Sodium hydroxide (NaOH) which are (8M, 10M, 12 M) are used with different solid-liquid ratio (1-1, 1-2, 2-1 and 3-1). For instance, 5g of metakaolin was used and mixed with 5ml of Sodium hydroxide solution. This experimental procedure then repeated with different solid liquid ratio in order to see which is the best option for the synthesizing the metakaolin geopolymers. Moreover, the mixture was stirred for 1 minute before poured into cubic moulds, and then was sealed to prevent water loss. The cubes were cured at 60°C for 24 hours. The dried materials was crushed and sieved to desired mesh size (125-250 µm). The prepared samples was stored in an airtight container for further use.

FIGURE 4.1. The synthesized and crushed Metakaolin acid based geopolymer

4.2 Characterization and analytical techniques

There are various analytical techniques were adopted in this studies. Several tests and analysis were carried out on geopolymer to determine the chemical compositions, surface structure, porosity and particle size using various tools. Besides that, fixed bed reactor will be used for hydrogen adsorption testing.

4.2.1 Chemical analysis using XRD

X-ray Diffraction (XRD) technique is used for a wide variety of material characterization studies. Primarily, the technique identifies crystalline species in material. In addition for compound identification, XRD can also be used to determine strain, preferred orientation, crystallographic structure, and grain size of crystalline materials. When x-ray diffraction is used in a glancing angle mode, crystalline structure as a function of depth can be obtained. The XRD spectra of the synthesis metakaolin in comparison with the different Molarity of Sodium Hydroxide (NaOH) of 8M, 10M and 12M as shown in Figure 4.2. Three main crystalline mineral phases were present in the fly ash namely quartz (SiO2), Sodium hydrogen silicate and Sodium Aluminium Silicate. The foaming agent (sodium hypochlorite solution, NaOH) used in the geopolymer synthesis process may have played a role in the formation of sodalite and halite phases seen in 8M, 10M and 12M.

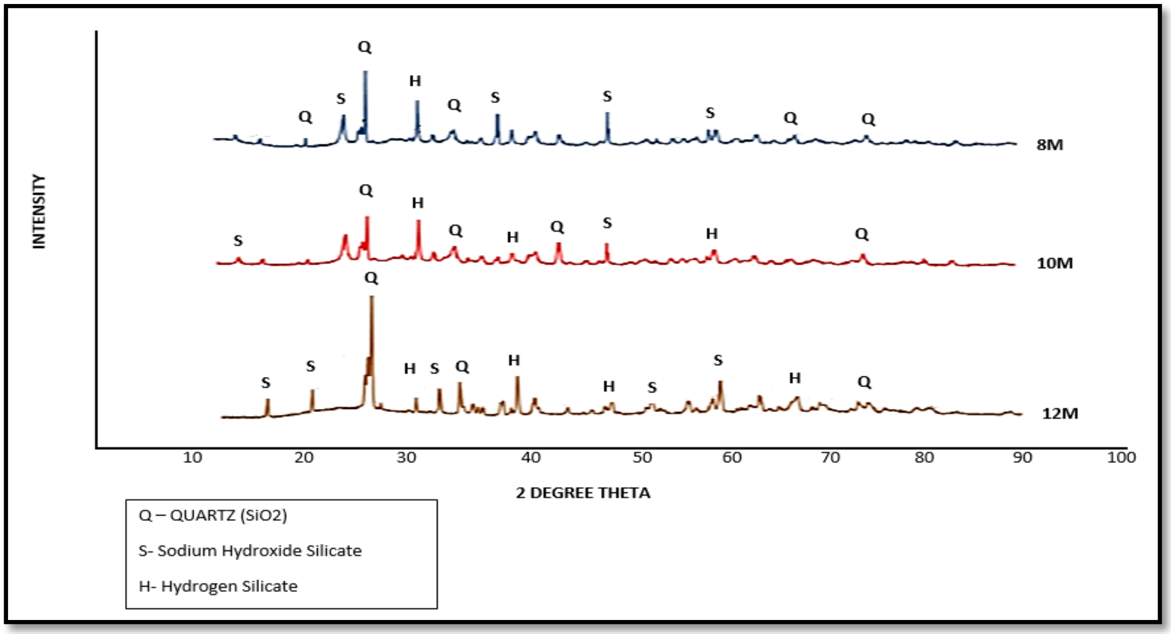


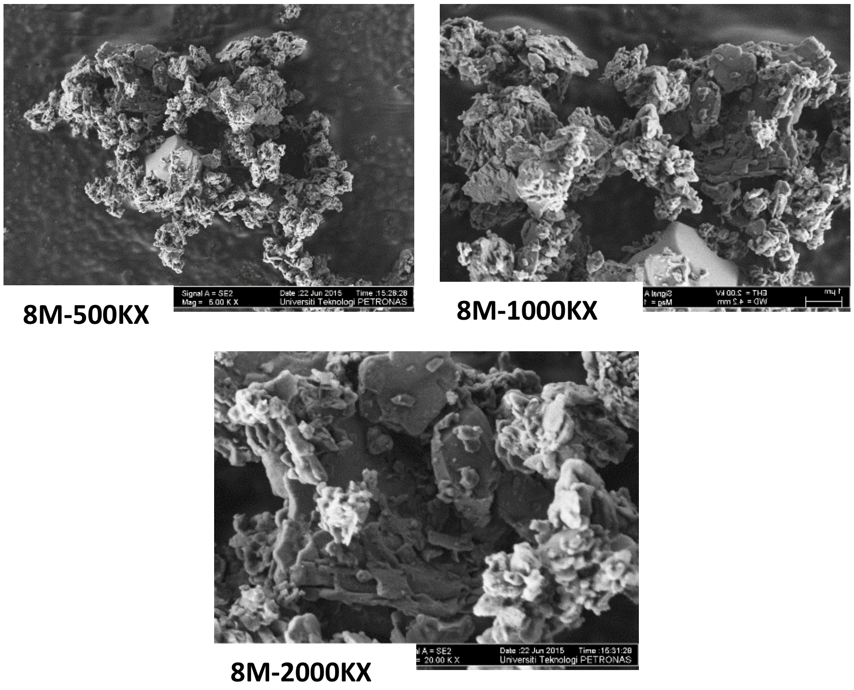
FIGURE 4.2. Graphs of Chemical composition 8M,10M and 12M of NaOH

Based on figure 4.2 shows that very few crystalline phases can be detected in the XRD of the synthesized Metakaolin , can be summarized that most of the material is amorphous. Based on the graph extracted from XRD test, a sharp peak at 26 theta can be seen due to the presence of amorphous silica and alumina in the synthesis metakaolin. After the decrease in quartz peak in geopolymer samples due to amorphous geopolymeric gel formation Moreover, the synthesize metakaolin is active and ended up in geopolymer formation with alkali activation because of amorphous structure.

4.2.2 Morphological analysis using FESEM

Figure 4.3 to 4.5 shows the surface morphologies of geopolymer in comparison with the synthesized metakaolin according to different molarities. It can be seen that different molarity of Sodium hydroxide (NaOH) used to synthesis the geopolymer consists of spherical particles with smooth outer surfaces. The morphology of the synthesized foamed geopolymer 8M, 10M and 12M consists of agglomerated particles and partially broken cenospheres. There is not much changes in morphological of geopolymer by increasing the molarity from 8M to 12M. These morphological changes observed in the geopolymer blocks are due to the dissolution of $SiO2$ and $Al2O3$(contained in the cenospheres) in alkaline solution leading to the formation of aluminosilicate gel which then acts as a precursor to geopolymer formation.

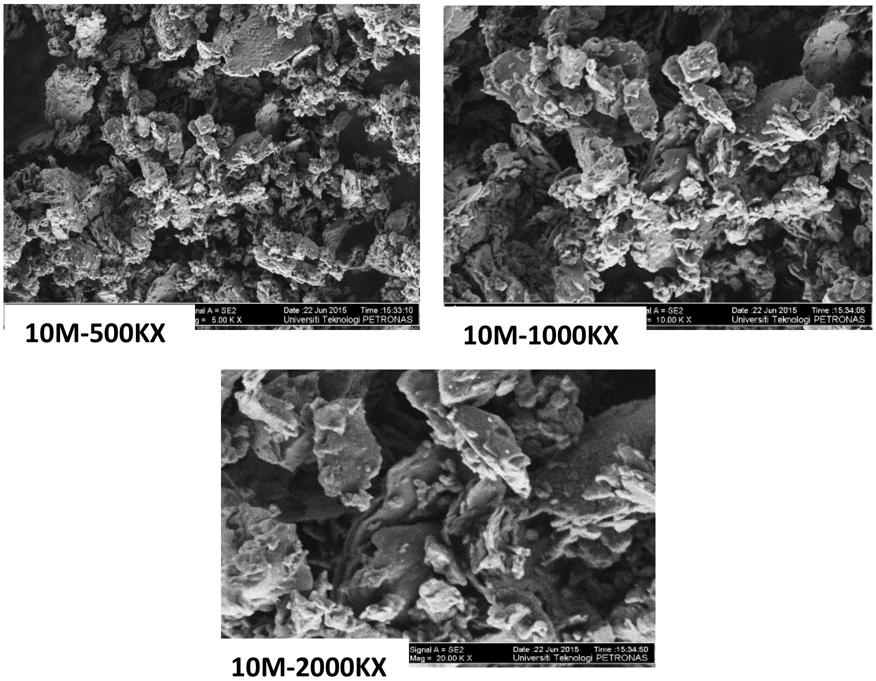
Metakaolin Synthesis acid based geopolymer according to different molarity of NaOH:



8M-500KX **8M-1000KX**

8M-2000KX

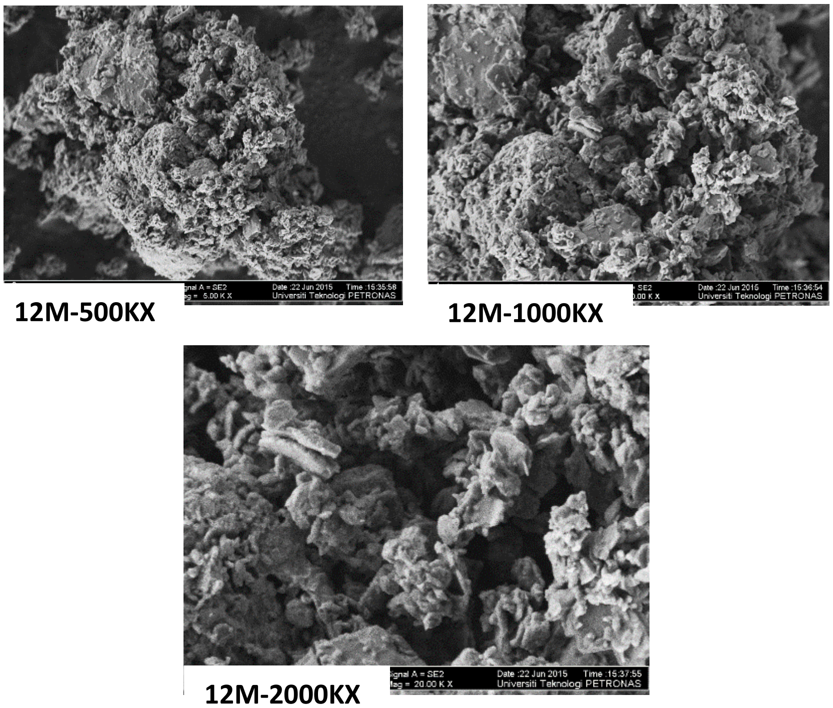
FIGURE 4.3. SEM micrographs of the foamed geopolymer blocks (8M-500KX, 8M-1000KX, 8M-2000KX).



10M-500KX **10M-1000KX**

10M-2000KX

FIGURE 4.4. SEM micrographs of the foamed geopolymer blocks (10M-500KX, 10M-1000KX, 10M-2000KX).



12M-500KX **12M-1000KX**

12M-2000KX

FIGURE 4.5. SEM micrographs of the foamed geopolymer blocks (12M-500KX, 12M-1000KX, 12M-2000 KX).

Based on figures 4.3, 4.4 and 4.5 explains that the microstructure of the geopolymer represented a mesoporous surface with pore sizes of 50–100 can be seen. Different types of morphologies were produced during geopolymerization. The porous structure as shown in figure and also suggest that synthesis metakaolin particles first disintegrate into nanoparticles and then are drained out by alkali activator, and proceeded to polymeric gel formation. Thus, Similar structures were observed in all figures above when using different NaOH (8M,10M and 12M) was used as activator to synthesis metakaolin geopolymer.

4.2.3 Pore Size Distribution and Porosity by Brunauer Emmette Teller (BET)

Brunauer-emmette-Teller (BET) analysis provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a surface area analyser. The technique encompasses external area and pore area evaluations to determine the total specific surface area in cm^2/g yielding important information in studying the effects of surface porosity and particle size in many applications. The surface isotherm adsorption curve graphs were plotted and shown as follows:

a) i) 8M for BET-Mesopore:

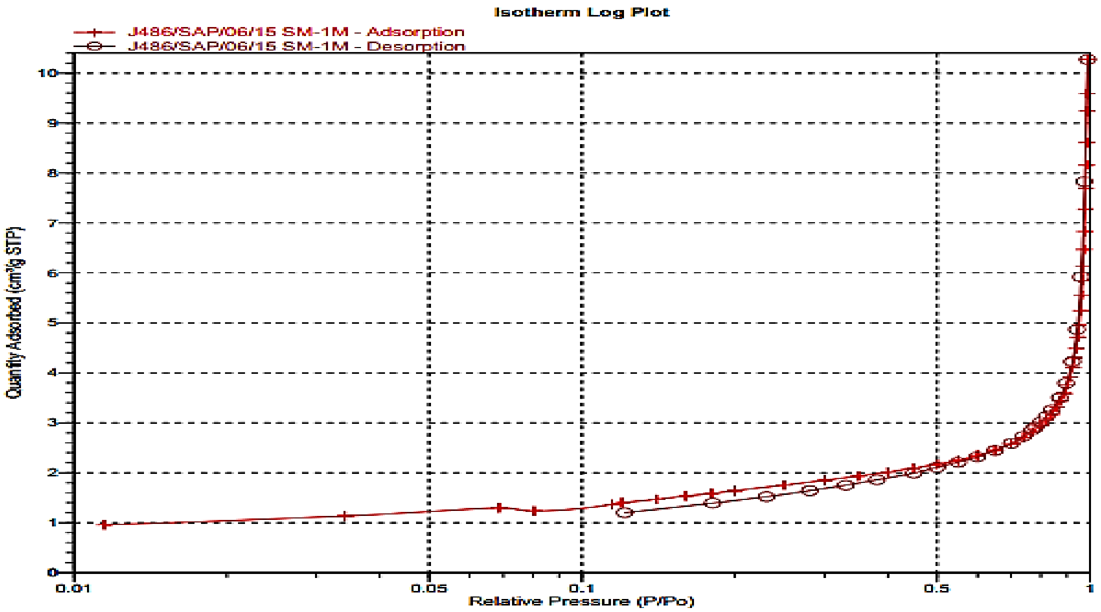


FIGURE 4.6. BET Surface Adsorption Isotherm of 8M (Mesophore)

Based on figure 4.6, adsorption isotherm curve was plotted based on quantity adsorbed with relative pressure (P/Po). For BET- Mesophore, the maximum quantity adsorbed for 8M of NaOH is 10.5 cm^3/g when it is approaching to constant relative pressure (P/Po).

ii) 8M for BET-Micropore:

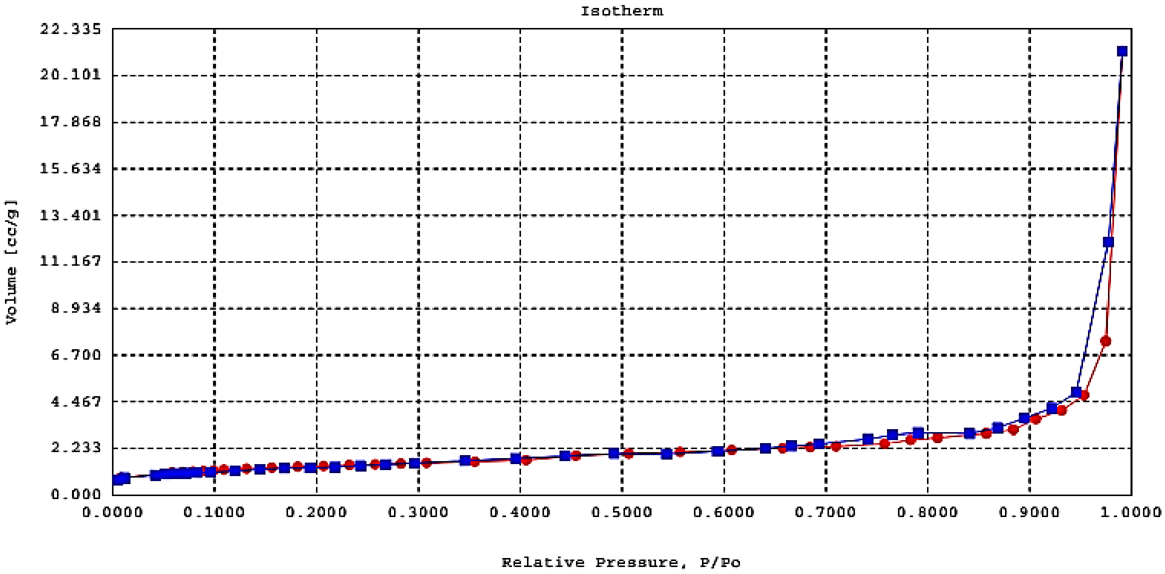


FIGURE 4.7. BET Surface Adsorption Isotherm of 8M (Micropore)

Based on figure 4.7, adsorption isotherm curve was plotted based on quantity adsorbed with relative pressure (P/Po). For BET- Micropore, the maximum quantity adsorbed for 8M of NaOH is 21.5cm^3/g when it is approaching to constant relative pressure (P/Po).

b) i) 10M for BET-Mesopore:

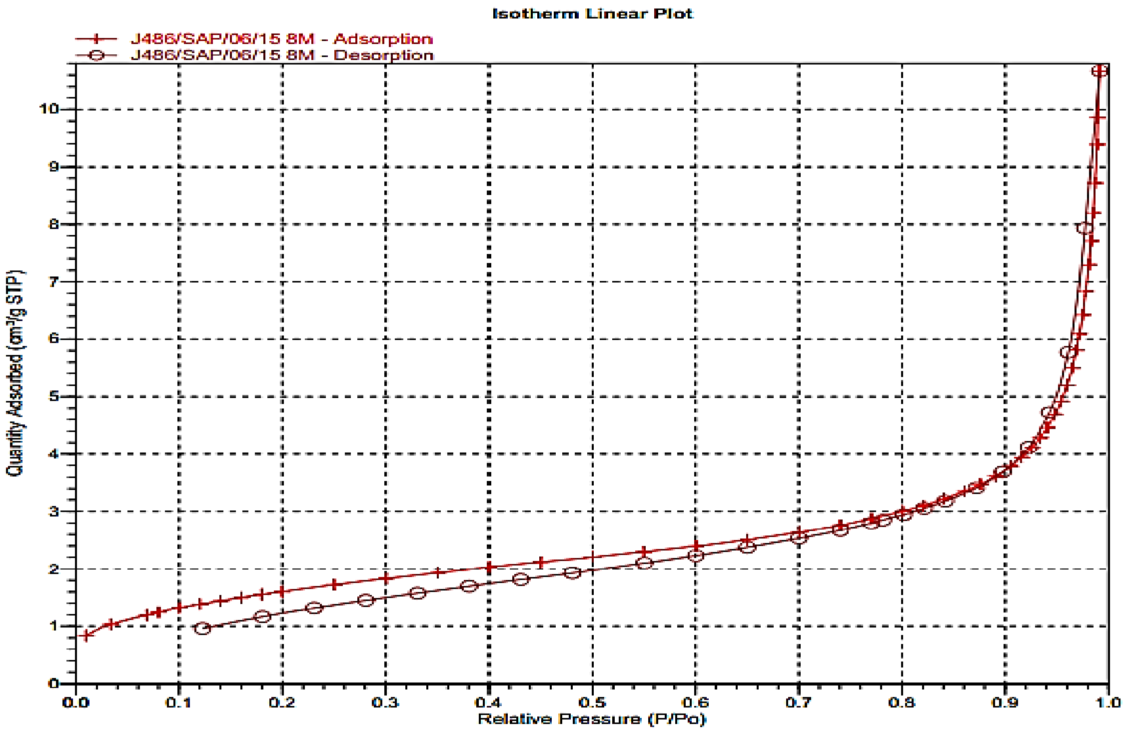


FIGURE 4.8. BET Surface Adsorption Isotherm of 10M (Mesophore)

Based on figure 4.8, adsorption isotherm curve was plotted based on quantity adsorbed with relative pressure (P/Po). For BET-Mesophore, the maximum quantity adsorbed for 10M of NaOH is 11.00 cm^3/g when it is approaching to constant relative pressure (P/Po).

ii) 10M for BET-Micropore:

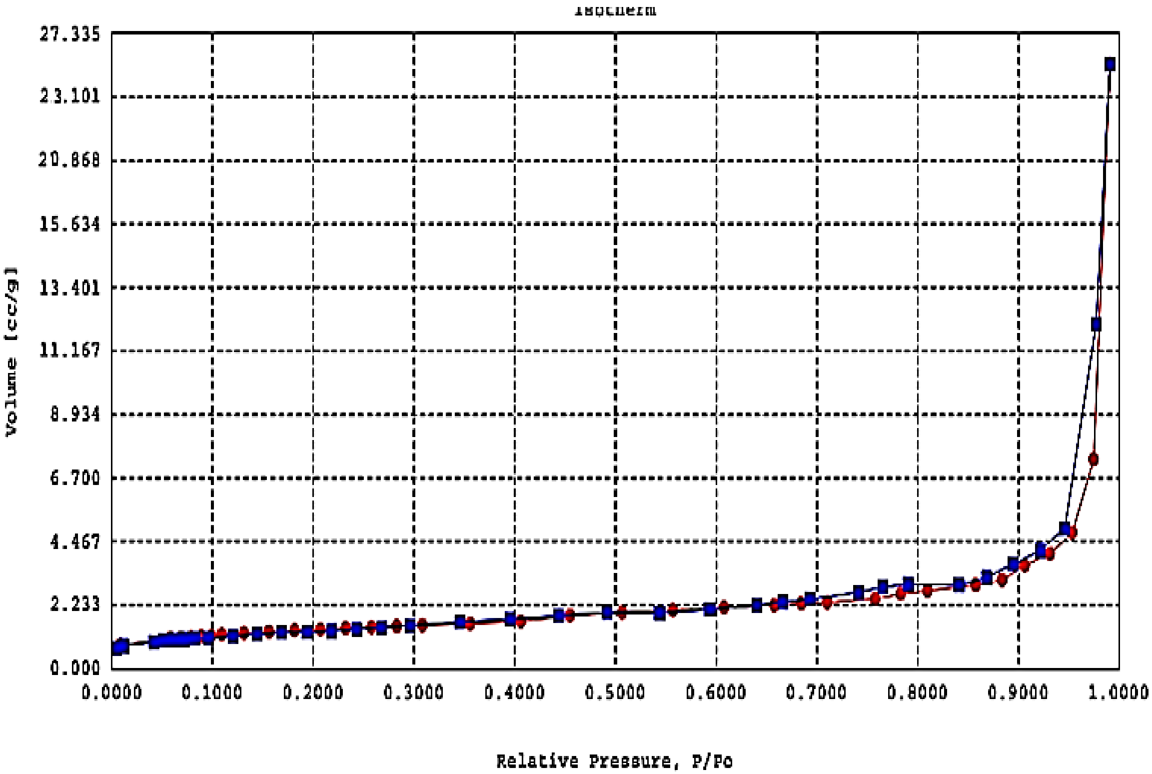


FIGURE 4.9. BET Surface Adsorption Isotherm of 10M (Micropore)

Based on figure 4.9, adsorption isotherm curve was plotted based on quantity adsorbed with relative pressure (P/Po). For BET-Micropore, the maximum quantity adsorbed for 10M of NaOH is 26.55 cm^3/g when it is approaching to constant relative pressure (P/Po).

c) i) 12M of NaOH used to synthesis metakaolin (Mesopore)

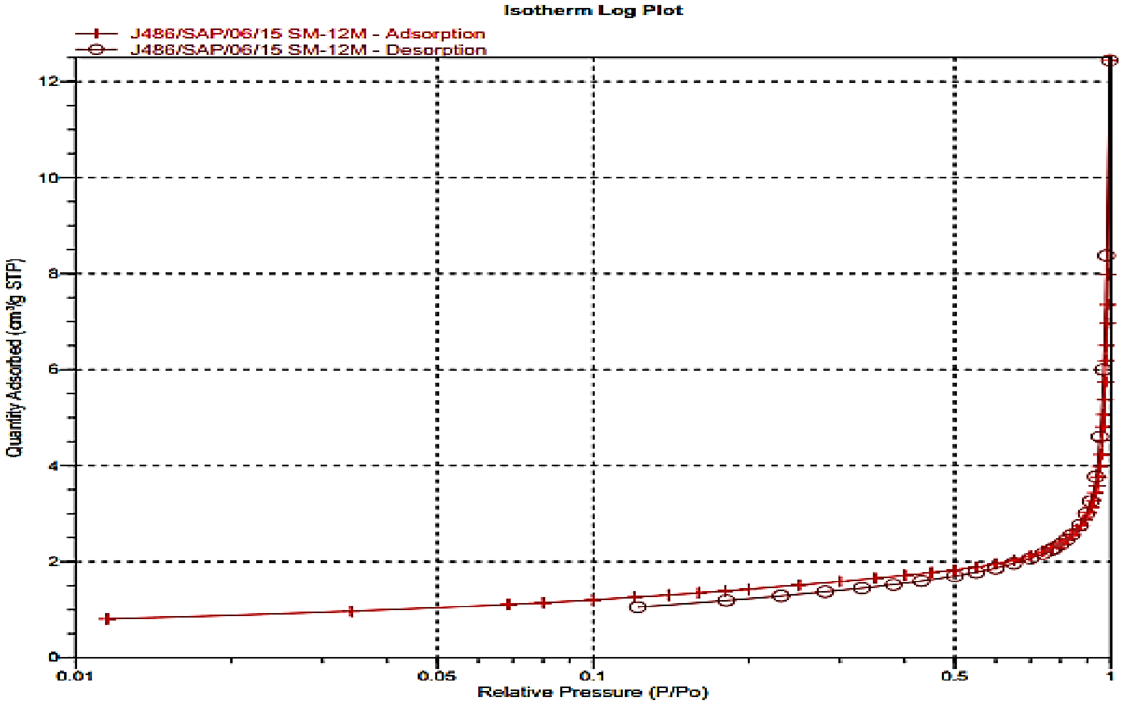


FIGURE 4.10. BET Surface Adsorption Isotherm of 12M (Mesopore)

Based on figure 4.10, adsorption isotherm curve was plotted based on quantity adsorbed with relative pressure (P/Po). For BET-Mesopore, the maximum quantity adsorbed for 12M of NaOH is 12.2 cm^3/g when it is approaching to constant relative pressure (P/Po).

c) ii) 12M of NaOH used to synthesis metakaolin (Micropore)

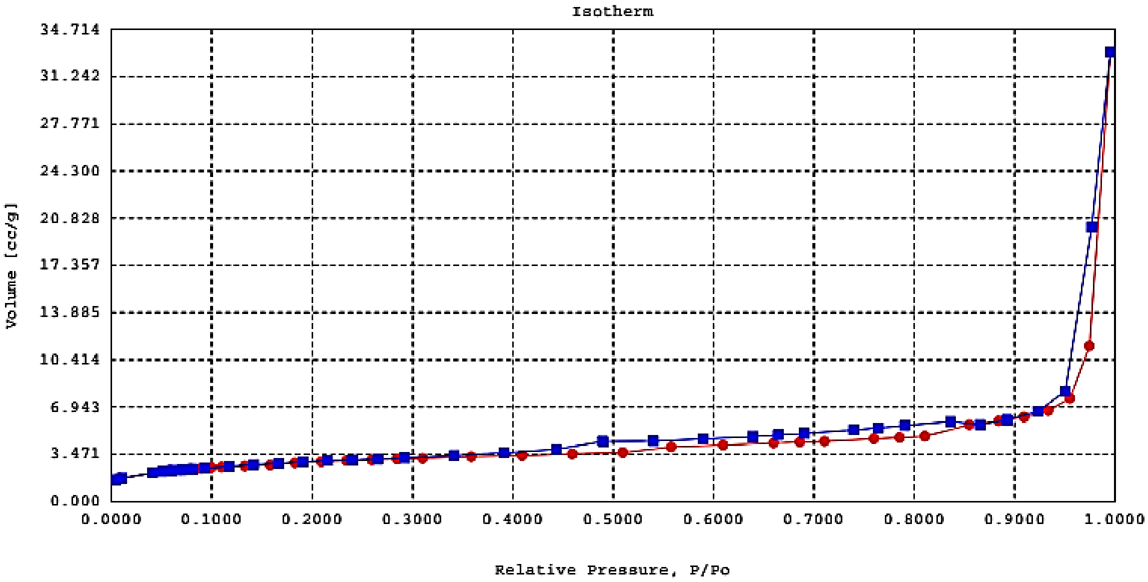


FIGURE 4.11. BET Surface Adsorption Isotherm of 12M (Micropore)

Based on figure 4.11, adsorption isotherm curve was plotted based on quantity adsorbed with relative pressure (P/Po). For BET-Micropore, the maximum quantity adsorbed for 12M of NaOH is 32.42 cm^3/g when it is approaching to constant relative pressure (P/Po). The table 4.1 below shows the BET-mesophore and micropore have been compared with different alkali activator of 8M, 10M and 12M. The relative pressure kept constant.

Alkali activator	Surface area (cm^2/g)	
	Mesophore	Micropore
SM-8M	10.5	21.5
SM-10M	11.0	26.55
SM-12M	12.2	32.42

Table 4.1. The surface area of BET-mesophore and micropore for different molarity.

4.3 Hydrogen Adsorption study

The hydrogen adsorption studies are currently done using the synthesized metakaolin with different alkali activator with the flow of 10% Hydrogen gas and 90% nitogen gas. After the hydrogen adsorption study is conducted, all the data are used to construct breakthrough curve graphs. The light blue region area on upper side of the breakthrough curve graph as shown in Figure 4.12 is the adsorbed amount of hydrogen.

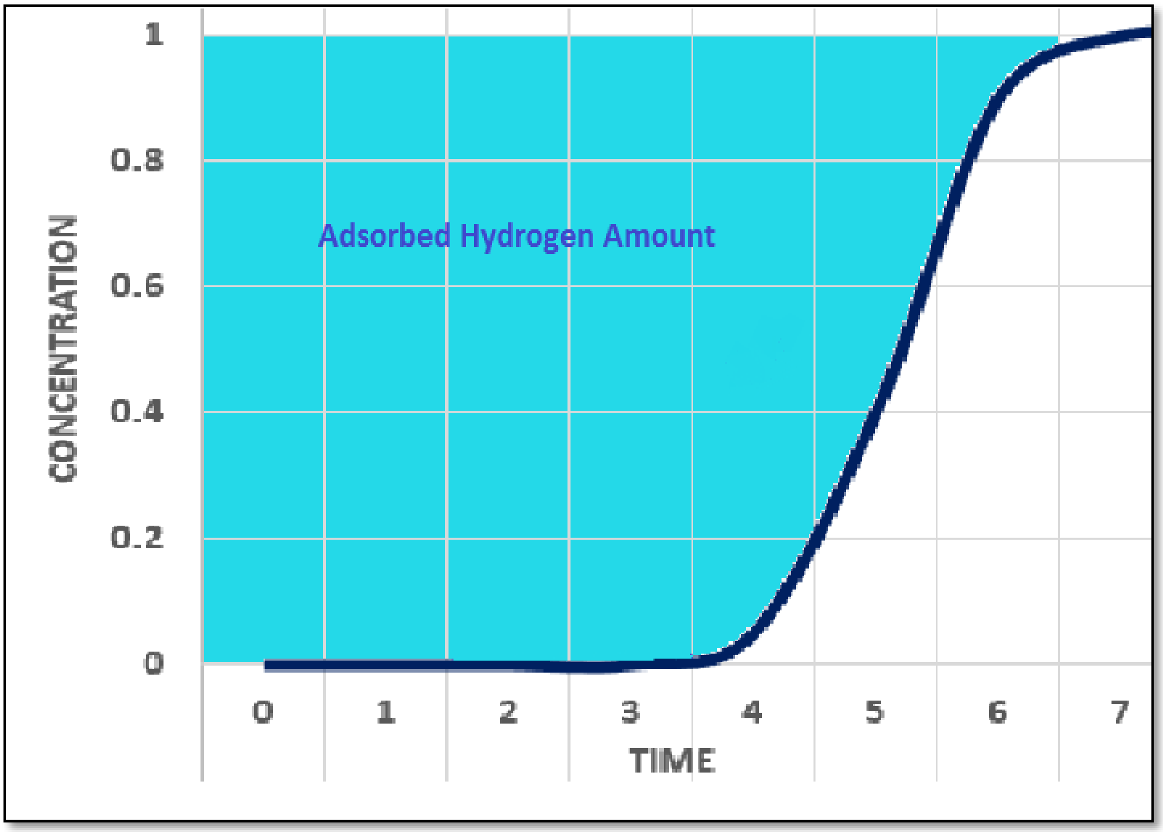


FIGURE 4.12. Adsorption breakthrough curve graph.

With the breakthrough curve, the capacity of the reactor for hydrogen adsorption can be calculated by using the following equation (Rodrigues, de Moraes Jr, da Nóbrega, & Barboza, 2007):

$$[1]\quad M_{ads} = \frac{Q_{t(MW)}}{\frac{RT}{P_A}} \left[\Delta t - \int_0^t \left(\frac{y}{y_o}\right) dt \right]$$

$$[2]\quad W = \frac{M_{ads}}{M_{bed}}$$

Therefore,

t = total adsorption time

y = initial concentration

y_o = final concentrarion

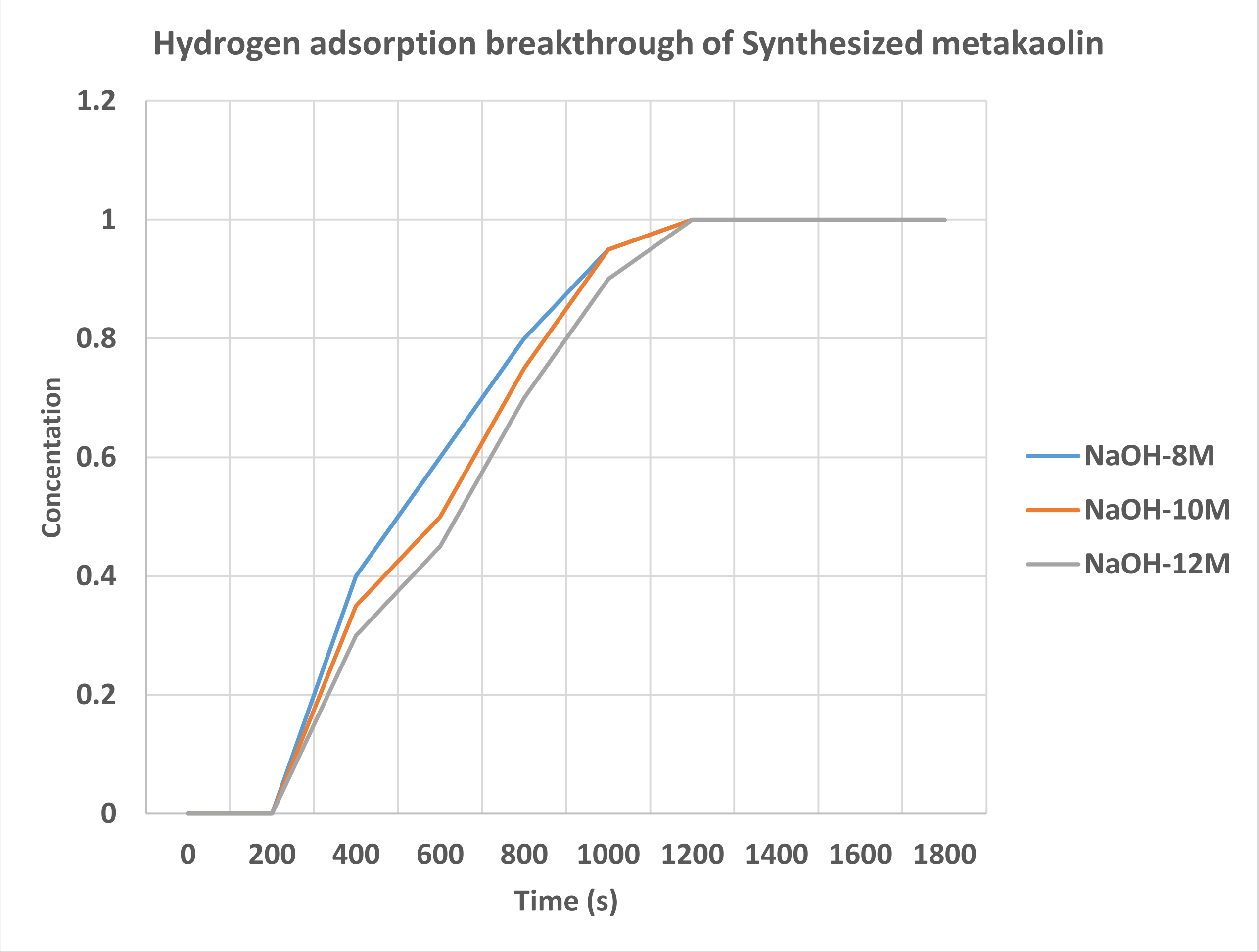
M_{ads} = adsorbed mass

Q_t = gas flow

p_A = partial pressure

M_{bed} = mass of bed = 0.5g

FIGURE 4.13. shows the test run of hydrogen adsorption done on the three samples:

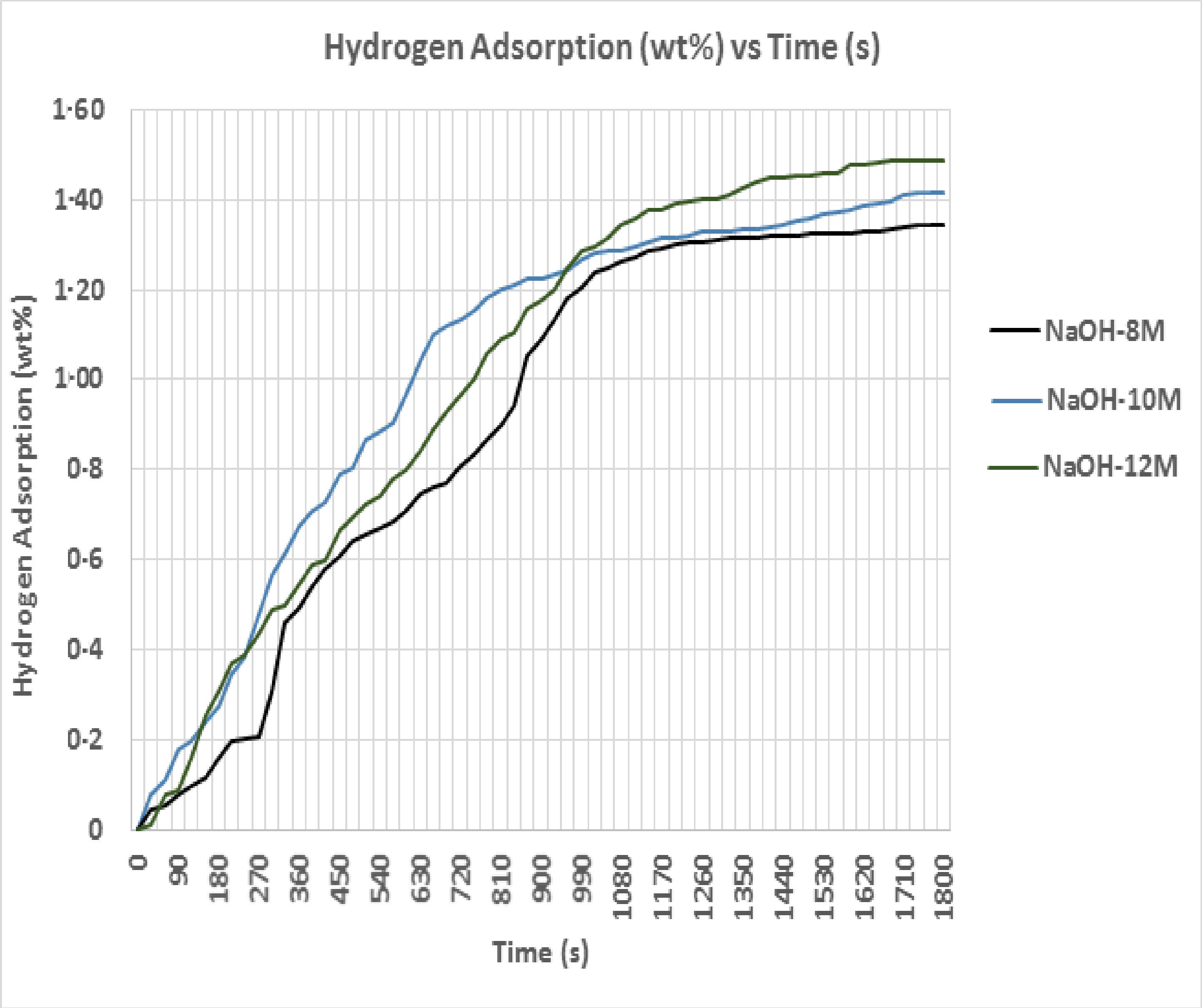


Using the equation proposed by Rodriques *et. al*, the amount of hydrogen adsorbed is calculated. Hence, the table below shows the hydrogen adsorbed amount and the weight percentage of adsorption.

Samples	**Mass of hydrogen adsorption (M_{ads})**	**Weight (%) of hydrogen adsorption (W_{ads})**
SM-NaOH(8M)	0.6720	1.344
SM-NaOH(10M)	0.7065	1.413
SM-NaOH(12M)	0.7440	1.488

TABLE 4.2. Mass of hydrogen adsorption and weight of hydrogen adsorbed by synthesized metakaolin.

FIGURE 4.14. below shows hydrogen adsorption (wt%) tests carried out on the three samples.



Based on figure 4.14, the graph of hydrogen adsorption was plotted in order observe which molarity of alkali activator suitable for maximum hydrogen adsorption uptake. From the hydrogen adsorption breakthrough for different alkali activator consists of 8M, 10M and 12M. The mass of the adsorption and weight percentage of the hydrogen adsorption as tabulated can be calculated from the adsorption breakthrough curve and equations proposed by Rodriques *et. al*. Based on the table above, the synthesized metakaolin with 12M NaOH has the maximum hydrogen adsorption uptake which is 1.49wt% compared to other alkali activator used. The 10M alkali activator used to synthesized metakaolin gives the average hydrogen adsorption uptake of 1.41wt% while the lowest alkali activator of 8M gives the lowest hydrogen uptake about 1.34wt%. It shows that when the alkali activator molarity increases during synthesis of the metakaolin, the hydrogen adsorption also increases.

In a nutshell, this increasing trend of weight percent signifies the amount of hydrogen being adsorbed in increasing. Thus, it can be justified that when the molarity of the NaOH increases, the porosity of the material also increases. Thus, when the porosity of the material increases, the hydrogen adsorption (wt%) increases as well. Hydrogen uptake of synthesized metakaolin alkali based geopolymer is also being compared with other adsorbent which is currently used as hydrogen adsorbent.

Comparison with other hydrogen adsorbent:

Samples/ Adsorbents	Synthesized metakaolin	Carbon nano-fibres
Pricing	Cheaper	Expensive
Source of synthesing	from industrial waste with alkali activator	Activated carbon with natural gas
Conditions	Temperature : 25^{o}C- 30^{o}C Pressure : 0.6 bar – 1 bar	Temperature : 25^{o}C- 30^{o}C Pressure : 0.6 bar – 1 bar
Maximum uptake (wt%)	1.488wt%	1.233wt%

TABLE 4.3. Comparison table with other hydrogen adsorbent

Based on table 4.3, the synthesized metakaolin is compared with hydrogen adsorbent which is Carbon nanofibres done by other researches. From the table above, it observed that the synthesized metakaolin gave the better hydrogen adsorption capacity compared to carbon nanofibres in term of pricing, source and also synthesizing method. Synthesized metakaolin should be preferred since it's cheaper due to it is derived from industrial waste. For Carbon nanofibres, although it's derived from waste activated carbon but in order to synthesis it, the procedure are long and complex. During synthesizing process, less energy required and also low CO_2 emmission. While comparing with carbon nanofibre adsorbents, the maximum hydrogen uptake for synthesized metakaolin is 1.49wt% than 1.23wt% that can be obtained from carbon nanofibre maximum hydrogen uptake.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The aim of this research is mainly to synthesis metakaolin with an alkali activator and then the synthesized geopolymer was then sent for characterization study by analytical techniques such as Brunauer Emmette Teller (BET) to find the pore size distribution, Field emission scanning electron microscopy (FESEM) to determine the surface morphology changes and X-ray diffraction (XRD) to identify chemical composition and amorphous of materials. Besides that, the hydrogen adsorption study carried out using synthesized metakaolin alkali based geopolymer by fixed bed reactor. The alkali activator used was sodium hydroxide consists of 8M, 10M and 12M are the three parameter used to synthesis metakaolin geopolymer. The hydrogen uptake was compared and analysed according to different molarity of alkali activator.The breakthrough curve for all the samples were analyzed and proves that hydrogen adsorption on least molarity of alkali activator (8M), it adsorbs about 1.34 weight percentage though slightly lower than alkali activator of 12M which has about 1.49 weight percent. As a conclusion, this research has been a success as all the objectives are fulfilled and it can be can adsorb hydrogen on highest molarity of alkali activator for synthesizing metakaolin alkali based geopolymer. Therefore, some recommendations for future research would be as following:

a) To use synthesized metakaolin acid based geopolymer using Phosphoric acid for hydrogen adsorption for future studies.
b) To use fly ash as a raw material to synthesize geopolymer instead of metakaolin because it is cheaper.
c) To change the molarity of the acid activator(by decreasing the molarity) in order to synthesize acid based geopolymer for better hydrogen adsorption.

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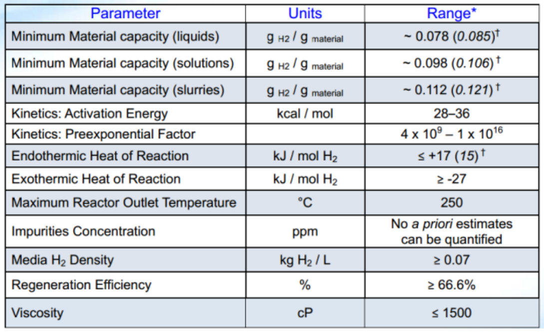
APPENDICES

Literature tables

<table>
<tr><th>Year</th><th>Author</th><th>Title</th><th>Criteria of good H_2 adsorbent</th><th>Material used And conditions</th><th>Result</th></tr>
<tr><td>2013</td><td>Donald Anton
Troy Semelsberger
Kriston Brooks
Don Siegel
Bruce Hardy</td><td>Hydrogen Storage Materials Requirements to Meet the 2017 On Board Hydrogen Storage Technical Target</td><td>
<table>
<tr><th>Parameter</th><th>Units</th><th>Range*</th></tr>
<tr><td>Minimum Material capacity (liquids)</td><td>$g_{H2} / g_{material}$</td><td>~ 0.078 (*0.085*)†</td></tr>
<tr><td>Minimum Material capacity (solutions)</td><td>$g_{H2} / g_{material}$</td><td>~ 0.098 (*0.106*)†</td></tr>
<tr><td>Minimum Material capacity (slurries)</td><td>$g_{H2} / g_{material}$</td><td>~ 0.112 (*0.121*)†</td></tr>
<tr><td>Kinetics: Activation Energy</td><td>kcal / mol</td><td>28–36</td></tr>
<tr><td>Kinetics: Preexponential Factor</td><td></td><td>$4 \times 10^9 – 1 \times 10^{16}$</td></tr>
<tr><td>Endothermic Heat of Reaction</td><td>kJ / mol H_2</td><td>≤ +17 (*15*)†</td></tr>
<tr><td>Exothermic Heat of Reaction</td><td>kJ / mol H_2</td><td>≥ -27</td></tr>
<tr><td>Maximum Reactor Outlet Temperature</td><td>°C</td><td>250</td></tr>
<tr><td>Impurities Concentration</td><td>ppm</td><td>No *a priori* estimates can be quantified</td></tr>
<tr><td>Media H_2 Density</td><td>kg H_2 / L</td><td>≥ 0.07</td></tr>
<tr><td>Regeneration Efficiency</td><td>%</td><td>≥ 66.6%</td></tr>
<tr><td>Viscosity</td><td>cP</td><td>≤ 1500</td></tr>
</table>
</td><td></td><td></td></tr>
<tr><td>N.D</td><td>California Institute of Technology,USA</td><td>Hydrogen Storage Materials</td><td>Adsorbed hydrogen does not chemically react during adsorption and, therefore, does not accumulate impurities which can poison the fuel-cell downstream. Because it does not involve bulk solid diffusion or chemical dissociation, the physisorption process is also extremely fast and fully reversible, allowing it to meet both the cycle-life and refilling-time targets. The fundamental problem with physisorption-based storage is that, due to the weak binding interaction between the H2 and the adsorbent surface, the hydrogen density at ambient conditions is too small.</td><td></td><td></td></tr>
</table>

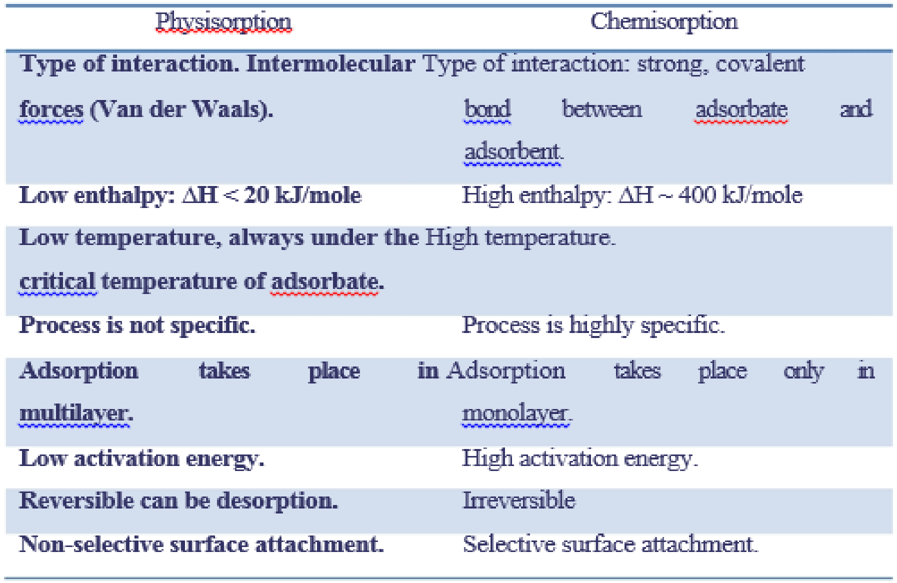
2012	M. Abdus Salam Suriati Sufian Ye Lwin	Hydrogen adsorption study on mixed oxides using the density functional theory	Reversible hydrogen storage systems adsorb hydrogen with the energy between physisorption and chemisorption where the hydrogen is stored predominantly in a molecular form. Those having lower formation energy require special conditions (high pressure or temperature) to adsorb hydrogen. Medium stable clusters are suitable enough to release or desorb hydrogen by less amount of energy (heat).	magnesium-nickel hydrides 250 or 300^{o}C (heated)	
2005	Andreas Züttel	Materials for hydrogen storage	Six storage methods currently being investigated, materials with either a strong interaction with hydrogen or without any reaction are needed. Besides conventional storage methods, i.e. high pressure gas cylinders and liquid hydrogen, the physisorption of hydrogen on materials with a high specific surface area, hydrogen intercalation in metals and complex hydrides, and storage of hydrogen based on metals and water are reviewed.		Hydrogen can be generated by reacting metals and chemical compounds with water. The common experiment, seen in many chemistry classes, where a piece of Na floating on water produces hydrogen, demonstrates the process.

2007	K.Mark Thomas	Hydrogen adsorption and storage on porous materials	Hydrogen storage is the main problem to be conquered for the successful implementation of fuel cell technology in transport applications and it represents a major materials science challenge. The methods of storage currently under consideration include high pressure gas, liquid hydrogen and adsorption on porous materials, complex hydrides and hydrogen intercalation in metals.	investigated on a wide range of carbon, silica, alumina, metal organic framework and polymer porous materials	Results indicate that up to ∼5 and ∼7.5 wt% of hydrogen can be stored on porous carbon and metal organic framework materials, respectively, at 77 K. The amounts of hydrogen adsorbed on porous materials at ambient temperatures and high pressures are much lower (≲0.5 wt%). The strong temperature dependence of hydrogen physisorption on porous materials is a limitation in the application of this method for hydrogen storage in addition to storage capacity requirements.

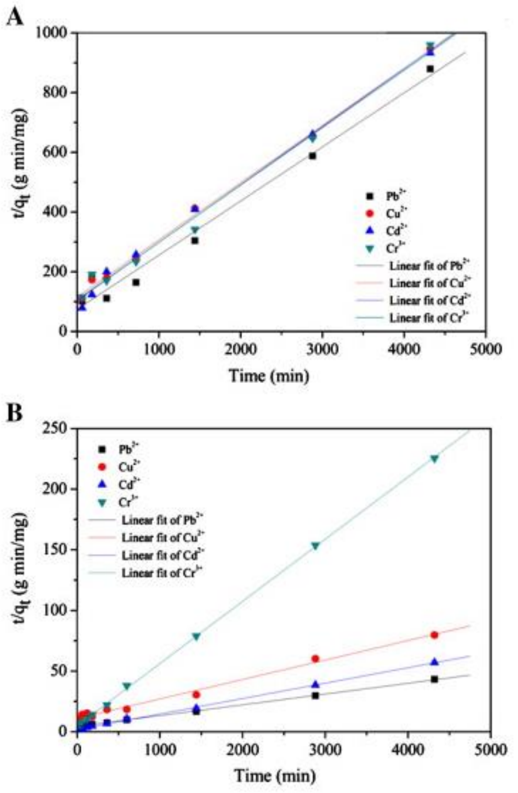
2013	Rizwan Wahab Farheen Khan Naushad Ahmad Hyung-Shik Shin,Javed Musarrat Abdulaziz A. Al-Khedhairy	hydrogen adsorption properties of nano and microstructures	The properties of hydrogen storage in materials were assessed for automotive applications, due to its low cost, high gravimetric and volumetric density, fast kinetics, proper thermodynamics and low temperature dissociation/decomposition properties, and long-term stability. Numerous metal hydrides, chemical hydrides, adsorbents, and the nano materials have been used for hydrogen storage purposes. Till date, the fulfillment of hydrogen storage criteria from these materials does not reach their high H_2 content. The hydrogen content is very less and it is below 6 wt%. Nanostructured materials have potential capacity due to their high surface area and adsorption properties on the surface and can easily influence thermo dynamics and kinetics of hydrogen adsorption .It can offer the possibility of controlling and tailoring the parameters independently of their bulk counterparts.	1)Nanoparticles (ZnO-NPs) 2)Microflower Composed with Thin Flakes (ZnO-TFs 3)Microspheres Composed with Tiny Nanoparticles (ZnO-MSs)	The hydrogen storage capacity of prepared nanoparticles of zinc oxide is ~1.220 wt%, whereas the storage capacity decreases in microflower composed with thin flasks (~1.011 wt%). There is a small change that appeared in hydrogen adsorption data microspheres composed with nanoparticles, which is ~0.966 wt%. From the data, it is evident that at higher surface area, the adsorption is higher. A comparatively higher adsorption in nanoparticles is probably due to higher surface area, and it decreases in micro-flower composed with thin flasks which provides an easy path way to hydrogen diffusion into the interstitial cavities and interlayer diffusion.

Year	Author	Title	Theory of adsorption	Type of adsorbent	Result
2001	A. Dabrowski	Adsorption from theory to practice	The adsorption of substrates is the first stage in many catalytic processes. The methods for separation of mixtures on a laboratory and on an industrial scale are increasingly based on utilising the change in concentration of components at the interface. Moreover, during the last 15 years new classes of solid adsorbents have been developed, such as activated carbon fibres and carbon molecular sieves, fullerenes and heterofullerenes, microporous glasses and nanoporous both carbonaceous and inorganic materials. Nanostructured solids are very popular in science and technology and have gained extreme interest due to their sorption, catalytic, magnetic, optical and thermal properties.	Carbon adsorbents - Active carbons - Activated carbon fibres - Molecular carbon sieves - Mesocarbon microbeads - Fullerenes - Heterofullerenes - Carbonaceous - Nano-materials Mineral adsorbents - Silica gels - Activated alumina - Oxides of metals - Hydroxides of metals - Zeolites - Clay mineral - Pillared clays - Porous clay hetero-structures PCHs Other adsorbents - Synthetic polymers - Composite adsorbents	

N.D	Amrita Laboratory universalizing education	Adsorption Isotherm	Types of adsorption: Depending upon the nature of forces existing between adsorbate molecules and adsorbent, the adsorption can be classified into two types: 1. **Physical adsorption (physisorption):** If the force of attraction existing between adsorbate and adsorbent are Vander Waal's forces, the adsorption is called physical adsorption. It is also known as Vander Waal's adsorption. In physical adsorption the force of attraction between the adsorbent and adsorbent are very weak, therefore this type of adsorption can be easily reversed by heating or by decreasing the pressure. 2. **Chemical adsorption (chemisorption):** If the force of attraction existing between adsorbate and adsorbent are almost same strength as chemical bonds, the adsorption is called chemical adsorption. It is also known as Langmuir adsorption. In chemisorption the force of attraction is very strong, therefore adsorption cannot be easily reversed.	Activated charcoal adsorbs gases like CO_2, SO_2, Cl_2 and etc. Pt or Ni metal kept in contact with a gas adsorbs the gas - Hydrogenation of oils. Animal charcoal, when added to acetic acid solution and shaken vigorously, adsorbs acetic acid. Molasses is decolorized by activated charcoal	
2012	KIM et al	Mechanism of adsorption	Mechanism of adsorption, first, the molecule diffusion process into the thin layer of the fluid or known as fluid film which is attached on the adsorbent. According to developing of diffusion, the second phase is the process which attached the vapor or gas along the pores. It is called as mixed diffusion because it consists of two diffusions which are pore diffusion and surface diffusion. The last process is the adsorption process in the pore adsorption site.		

2006	Jaafar & Nhatasha,	Physisorption and Chemisorption			

Physisorption	Chemisorption
Type of interaction. Intermolecular forces (Van der Waals).	Type of interaction: strong, covalent bond between adsorbate and adsorbent.
Low enthalpy: $\Delta H < 20$ kJ/mole	High enthalpy: $\Delta H \sim 400$ kJ/mole
Low temperature, always under the critical temperature of adsorbate.	High temperature.
Process is not specific.	Process is highly specific.
Adsorption takes place in multilayer.	Adsorption takes place only in monolayer.
Low activation energy.	High activation energy.
Reversible can be desorption.	Irreversible
Non-selective surface attachment.	Selective surface attachment.

Year	Author	Title	Geopolymer as potential adsorbent	Meterials used	Result
2011	T.W Cheng M.L.Lee M.S. Ko T.H Ueng S.F Yang	The heavy metal adsorption characteristics on metakaolin based geopolymer	The adsorption efficiency of the geopolymer for different heavy metals. Geopolymer could adsorb heavy metals, having the best adsorption for Pb^{2+}. Adsorption dynamics fit the pseudo-second-order kinetic model well. Both physical adsorption and chemical bonding are containing the adsorption mechanism.	1) Sodium silicate (weight ratio SiO_2:Na_2O = 3 .3, weight % Na_2O = 6–7% and SiO_2 = 23–25%) 2)10 M NaOH (analytical grade) with a molar ratio of SiO_2/Na_2O = 1 .0	 Fig. 3. Linear fitting of experimental data to pseudo-second order equation. (a) pH < 2 and (b) pH = 4.

2013	Satoshi Sugita, Motohiro tagaya, Akaomi kobayashi	Metakaolin based geopolymers for targeted adsorbents to heavy metal ion separation	Cs^+ and Pb^{2+}, from other heavy metal ions mixture. The geopolymer was optimized at Si/Al = 2 as adsorbent, targeting to Cs^+ and Pb^{2+} separation. The binding behavior was well fitted to Langmuir model, which proved that the metakaolin-based geopolymer had multi binding to adsorb ions. The effective adsorption was also observed independent of NaCl concentration for the Cs^+ and Pb^{2+}. This meant that the ion adsorption of geopolymers occurred under non-electrostatic mechanism.	1)Silica 2)Metakaolin 3)Al, Si component	

2005	Davidovits,	Geopolymer application	Geopolymers have been used in many applications and one of the major applications is in the construction industry. This is due to its quick curing time and high tensile strength. Other applications of the geopolymers include archaeology and heavy metal adsorption. Geopolymer can be synthesized easily under normal ambient condition using different raw materials, for instance metakaolin and fly ash. Metakaolin is simply a heated kaolin which also known as china clay while fly ashes are waste from thermal power factories. Both raw materials have high aluminosilicate and highly favourable to synthesize geopolymers.		

2002	Xu & Van Deventer,	Geopolymerization	The basic step of geopolymerization is the dissolution of the solid aluminosilicate oxide in a KOH or NaOH solution to form SiO_4 and AlO_4 tetrahedral units. It is newly developing field of research which provides a mature and cost effective 32 solution to many problems by utilizing solid wastes or byproducts where hazardous residue has to be stored under critical environmental conditions		

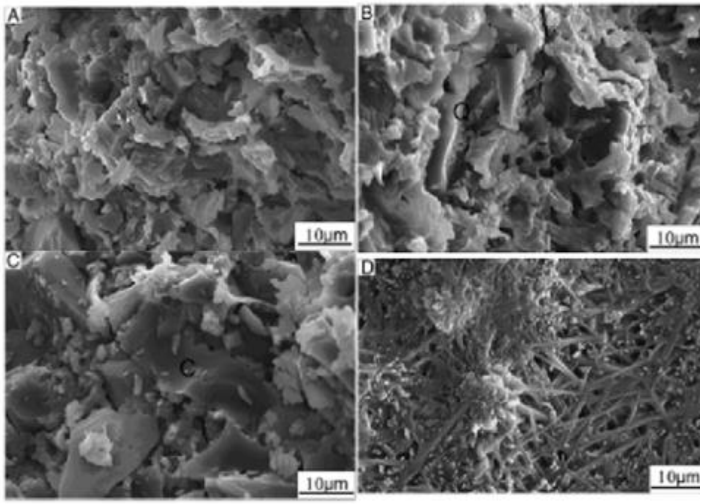
Year	Author	Title	Metakaolin	Condition	Result
2009	Nkoumbou et al	Sources of metakaolin	Main sources of metakaolin are either kaolin or paper sludge after suitable treatment. Kaolin is one of the most widely used industrial minerals where its world's total output exceeds 25 million tonnes		
2005	Kostuch, Walters Jones	Metakaolin	Metakaolin is essentially an anhydrous aluminisilicate that is produced by the thermal composition of (Duxson, Mallicoat, Lukey, Kriven, & Van Deventer, 2007), a naturally occurring clay containing kaolinite, $Al_2Si_2O_5(OH_4)$ and trace amounts of silica and other minerals.		
2007	Duxson, Mallicoat, Lukey Kriven, Van Deventer	Metakaolin and its properties	A naturally occurring clay containing kaolinite, $Al_2Si_2O_5(OH_4)$ and trace amounts of silica and other minerals.The hydroxyl ions are strongly bonded to the aluminisilicate framework structure, thus only temperature in excess of 550^{o}C can eliminate them. When large-layer structured materials such as kaolinite are subjected to intensive thermal treatment (850^{o}C), the material undergoes series of transformation that enhance it subsequently reactivity with given chemical agents. At approximately 600^{o}C, kaolinite loses most of its crystallinity. This implies that the hexagonal layer structure in		

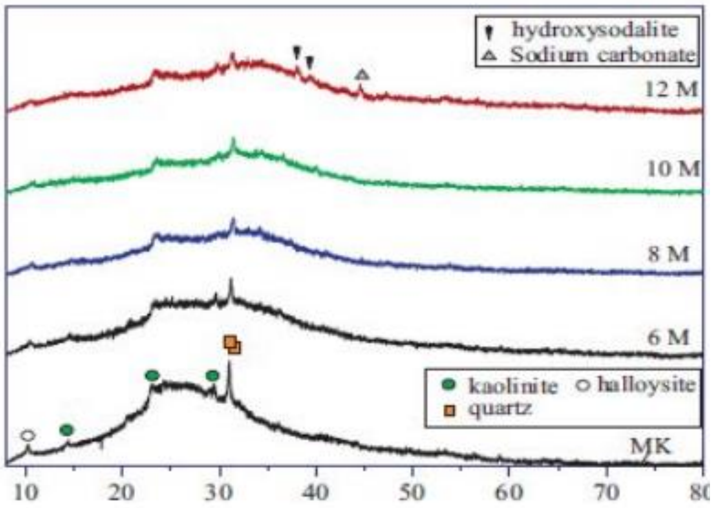
			kaolinite is partially destroyed at this temperature. The original mineral structure becomes disorganized, forming the material referred to as metakaolin. Metakaolin is a partially ordered structure that cannot rehydrate in the presence of water or dies so very slowly		

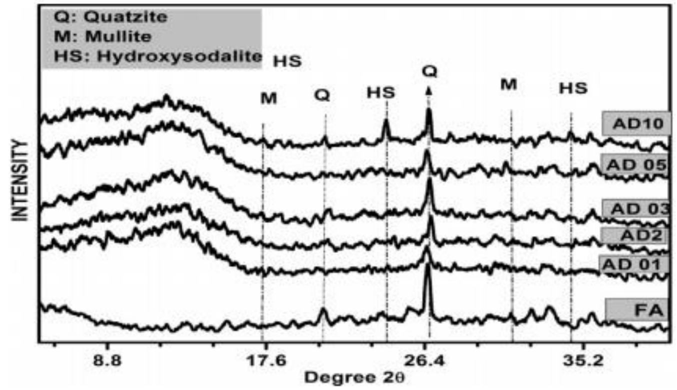
Year	Author	Title	Alkali activator	Condition	Result
2004	Phair Van Deventer Smith	Alkali activator	Alkali activators can be divided into two groups which are alkali hydroxide which meant for dissolution of raw materials, and sodium (or potassium) silicate solution which acting as a binder		
2007	Khale Chaudhary	Strong alkali	Strong alkalis are required to activate the silicon and aluminium present raw material. Alkali metal salts and/or hydroxide are necessary for the dissolution of silica and alumina as well as for the catalyst of the condensation reaction. The common activators are NaOH, Na_2SO_4, Na_2CO_3, K_2SO_4, KOH or a little amount of cement clinker. Sodium silicate has been used for more than a century for the production of commercial products such as special cements, coatings, molded articles and catalysts. The soluble silicate is		

			mixed with solid raw materials or other source of multivalent metal ions that promotes the gelation and precipitation of silicates. The more the NaOH get in contact with the reactive solid materials, the more silicate and aluminate monomers are released.		

Year	Author	Title	Type of geopolymer	Condition	Result
2010	Le-Ping et al	Phosphorous cid based geopolymer	Phosphorous acid-based geopolymers formed are amorphous, porous and displayed excellent thermal stability. Even though there is no research being done on the application of phosphoric acid-based geopolymer, the proven porous properties have made them a potential adsorbent material.		
2010	Le-Ping et al	Synthesis of Phosphorous Acid-based Geopolymer	Metal powder such as Al and Fe can be added as a pore-forming agent. This work done have shown that the geopolymers formed will possess different properties as the component ratios are altered. For instance, the amount of pore-forming agent has an effect on the porosity and compressive strength of the synthesized geopolymer. The higher the Al content, the higher the porosity of the sample and the lower the compressive strength. It is also reported that the lower water content will result in higher viscosity and smaller final pore size. However, if the water content is too high, the viscosity will be quite low and lead to the disappearance of all pores.		

Year	Author	Title	Analytical techniques	Result
2012	Liu, Cui, He, Liu, & Gong,	Characterization of geopolymer	The surface structure of phosphoric acid-based geopolymer is determined using Scanning Electron Microscopy (SEM). SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of the solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that display spatial variations in these properties.	 SEM micrographs of geopolymer heated for 1 h at various temperature: (A) 150ºC, (B) 1050ºC, (C) 1450ºC, and (D) 1550ºC

2012	Zhang et al	X-Ray Diffraction	X-ray Diffraction (XRD) is used for a wide variety of material characterization studies. Primarily, the technique identifies crystalline species in material. In addition to compound identification, XRD can also be used to determine strain, preferred orientation, crystallographic structure, and grain size of crystalline materials. When x-ray diffraction is used in a glancing angle mode, crystalline structure as a function of depth can be obtained.	 Co Kα radiation XRD patterns of MK and its geopolymerization products after activation with NaOH solution of 6-12 mol/L at 30^{o}C for 72 h (Zhang et al., 2012).

2014	M. Irfan Khan, Khairun Azizlin Suriati Sufian, Zakaria Man	Sodium silicate-free geopolymers as coating materials: Effects of Na/Al and water/solid ratios on adhesion strength	The X-ray diffractograms of selected geopolymers and theirstarting materials are shown in Fig. 8. Given the amorphousnature of the geopolymers, characterization using XRD is atedious work [43]. Very few crystalline phases can be detected in the diffractogram of the fly ash, thereby confirming thatmost of the material is amorphous. A broad mound at 20–30 shows the presence of amorphous silica and alumina in the fly ash. The amorphous content in thefly ash is chemically active and results in geopolymer formation upon alkaline activation. Two types of fly ash particles can be found in the polymer matrix, the unreacted and partially reacted particles. Most of then, large particles remained unreacted. Fig. 9(b and d) shows the magnified surface of a partially reacted fly ash particle. This pattern explains the disintegration mechanism of large particles into nanoparticles during geopolymerization reaction. The results suggest that fly ash particles first disintegrate into nanoparticles and then are leached out by alkali activator, there by leading to polymeric gel formation.	 Fig. 8. X-rays diffractograms (XRD) of fly ash and selected geopolymers.