Synthesis and Characterization of Nano Silica from Local Siliceous Sand

by

Nurulizzah Ishak

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

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Prof. Murugesan
Project Supervisor

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
July 2010

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.

NURULIZZAH ISHAK

ABSTRACT

A commercial silica (SiO_2) powder was synthesized using a chemical reaction. The method of preparing silica nanoparticles from siliceous sand comprises: grinding the siliceous sand; solving siliceous sand with sodium hydroxide to form sodium silicate aqueous solution; neutralizing an aqueous solution of sodium silicate with hydrochloric acid to form precipitate; washing to remove chlorine; drying the nano silica and grind the nano silica powder. Furthermore, the nano silica surface was treated with surfactant hexamethyldisilazane (HMDS). The yield for different reaction time of siliceous sand with sodium hydroxide was calculated. Moreover, the structure, particle size distribution and morphology were determined by Fourier Transform Infrared Spectrometry (FTIR), Particle Size Analyzer, Scanning Electron Microscopy (SEM) and X-Ray Distribution (XRD). The result showed that the yield of sodium silicate solution is higher with the present of glycerol (more than 80%) and increasing with reaction time. SEM results show that nano silica is agglomeration form with the dimension of 96 nm. However, after treated with HMDS, the nano silica forms less agglomerate with average size of 88 nm. The FTIR spectrum confirms that the HMDS modifier is incorporated on the surface of SiO_2 particles. XRD pattern of nano silica confirms the amorphous nature of the nano silica compared before synthesis which is in crystal structures.

ACKNOWLEDGEMENT

First and foremost, highest thanks to The Almighty, the source of my life, wisdom and hope for giving me the strength and patience to pursue and complete this Final Year Project in blue colors.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF THE STUDY

Recently, many activities have growing the need for development of a method for removing large quantities of oils from the surface of water bodies such as lakes, rivers and oceans. For example, on April 2010, the most horrific incident occurred around Gulf of Mexico. The leakage of oil from the wellhead affecting the human and environment around. Figure 1.1 shows the view of the spill released in Gulf of Mexico.

Figure 1.1: The View of the Oil Spill in the Gulf of Mexico (Tom & Deborah, 2010)

The dispersed oil, even in microscopic droplet form, was highly toxic to human and animals. Numerous solutions have been proposed for dealing with the problem of discharged oil from water which occurs mostly due to the human faulty. For example, the incident of oil tanker accidents at sea or mishap in the loading of oil from tankers. Such floating oil creates great damage to the water and to the surrounding shorelines (Peterson et al., 2003).

The three most common technologies used to remove contaminants from water are biological, chemical, or physical treatment. Compared to biological or chemical treatments, physical treatment methods may offer an acceptable alternative since the adsorbents can be reuse for several cycles. Physical treatment using physical forces rather than chemical break down. The best method for separation of hydrocarbons is adsorption process (Štandeker et al., 2007) where contaminents is drawn into the adsorbent material in same way water is drawn into a sponge (Warrenchak & Phelan, 1991).

Adsorbents have been the primary materials used for removal of impurities usually have unique properties such as high surface areas and small pores, such as micropores and mesopores. According to International Union of Pure and Applied Chemistry (IUPAC), micropores is diameter of hole below 2 *nm* while mesopores with diameter greater than 2 *nm* and smaller than 50 *nm*. Pore size, pore distribution, and surface area, as well as pore surface chemistry, are the major factors in the adsorption process (Štandeker et al., 2007).

Nanoparticles have two key properties that make them particularly attractive as sorbents. On a mass basis, they have much larger surface areas than bulk particles. Nanoparticles can also be functionalized with various chemical groups to increase their affinity towards target compounds (Nora & Mamadou, 2005).

Unmodified and modified porous silica are widely used in various areas of modern science and technology as adsorbents. The range of applications of porous silica is continuously growing due to their unique properties, such as high specific area, large pore volume, precisely specified size of pores and particles, large mechanical and thermal stability, and easy for surface modification (Choma et al., 2003). Moreover, the solid organic materials employ for synthesis the nano silica commercially available in large quantities and at low cost. Moreover, silica is nontoxic and biocompatible for research (Jin et al., 2009).

Nano silica is applicable in various fields. For example as the filler for semiconductor, encapsulants, the materials for improving the durability of paints and ink and the materials for optical fibers, ceramics and glass industries (Liou, 2004).

1.2 PROBLEM STATEMENT

However, the problem using amorphous silica is that it is normally hydrophilic and oleophilic because of the existance of Si-OH functional group (Warrenchak & Phelan, 1991). It has now been found that a solid adsorbent prepared with the presence of a modifier which may be either a single chemical compound or a group of compounds will result for better properties. The adsorbent may possess a specific adsorption which is closely related to the modifier. The adsorption capacity of the modified adsorbent is also generally higher that the unmodified adsorbent.

The hydrophobicity of the nano silica can be achieved by surface chemical modification of the nano silica by incorporating certain chemical additives in the silica surface (Belyakova & Varvarin, 1999)(Štandeker et al., 2007). Chemical surface modification can be categorized as follows (Ahn et al., 2004):

1. Surface modification by chemical reaction. This type of surface modification promotes a chemical reaction between the polymer matrix and modifier to strengthen the adhesion.

2. Surface modification by a nonreactive modifier. A nonreactive modifier reduces the interaction between the particles within agglomerates by reducing the physical attraction rather than by any chemical reaction. Stearic acid has been widely used as a non interacting surface modifier.

1.3 OBJECTIVES OF STUDY

- To synthesis nano silica from local siliceous sand by using precipitation method.
- To investigate the effects of varying reaction time of sand and sodium hydroxide with yield.
- To study the properties of nano silica by various analytical tools such as FTIR, XRD and SEM.

1.4 PREFACE

The first chapter of this report is a brief introduction to this project and the discussion on the current situation related to the project. The separation of oil from water by using the adsorbent is a main focus of the project. The problem statement and objectives are discussed deeply in Chapter 1. Chapter 2 presents the basic theory of properties of adsorbent, concept of hydrophobicity and discussion on the silica as the adsorbent. The methods of preparing nano silica and the characterization result from previous study are also discussed in second chapter.

Chapter 3 outlines the experimental work of the research. It consists of methodology of preparing powder form of siliceous sand, synthesis of nano silica by precipitation method, silica surface modification and list of chemicals and equipments used for experimental work. Chapter 4 presents the result and discussion from XRD, FTIR and SEM-EDS study. Chapter 5 is the conclusion and recommendation for further work. The figure of the samples and experimental work are attached in Appendices.

CHAPTER 2

LITERATURE REVIEW

2.1 ADSORBENTS

Adsorbents that have been the primary materials used for removal of impurities for both water and air purification (Štandeker et al., 2007). In the evaluation of solid adsorbent for separating one or more compounds from a mixture of compounds, two characteristics of the adsorbent are employed, namely, specificity or selectivity and adsorptive capacity. The preferred adsorbents generally have a high specificity for the particular compound to be separated from the mixture and a low adsorption capacity for other compounds of the mixture. The resulting adsorbent has low production cost, high capacity and fast kinetics for adsorption applications.

Granular activated carbon (GAC) is a widely used adsorbent due to its high adsorption capacity and availability (Li et al., 2002). However, GAC display disadvantages such as low selectivity, limited modification flexibility less than 100% working capacity and costly for reactivation (Liu et al., 2009) (Štandeker et al., 2007). Thus, an alternative adsorbent with a better surface property is needed to overcome the limitation associated with GAC.

In order to effectively remove toxic or oil from water it is necessary that the adsorbent adsorb only the toxic and not the water. The material should possess excellent oleophilic and hydrophobic characteristics. Based on studied, nano silica has been known to exhibit both these properties (Warrenchak & Phelan, 1991). Silica has surface silanol groups, which can function as anchoring groups for variety chemicals through surface chemical reactions.

2.2 HYDROPHOBIC AND HYDROPHILIC

Hydrophobic and hydrophilic forces are interactions that serve to keep chemical groups positioned close to one another.

Hydrophobic (water hating) interactions are created because of the uncharged nature of the involved chemical groups. An example of such a chemical group is CH_4. All the bonds around the carbon atom are occupied. The chemical group is described as being nonpolar. Thus, a water molecule, a polar molecule is unable to establish an association with the non-polar chemical group. This tends to create instability in the network of water molecules, and so is undesirable. The repulsive force of the surrounding water molecules acts to force hydrophobic regions into an association with like regions (Lerner & Lerner, 2006).

Hydrophilic (water loving) interactions are possible with polar chemical group. Water is polar because oxygen is far more electronegative than hydrogen and thus the electrons involved in an oxygen-hydrogen bond spend more time in proximity to the oxygen atom. Because of this unequal electron sharing, the oxygen atom takes on a partial negative charge and the hydrogen atom a partial positive charge. In addition, the bonds in a water molecule (oriented at 105° in a "bent" molecular shape) cannot cancel each other out. Other polar groups can then form ionic type bonds with water. Regions of proteins and other biological materials that are exposed to the environment are typically hydrophilic (Lerner & Lerner, 2006).

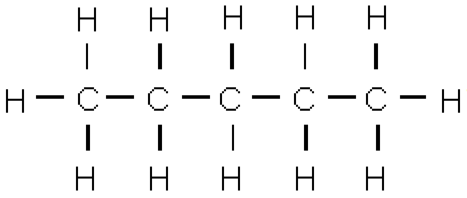


Figure 2.1: Bonding of Non-polar Molecules (Hydrophobic)

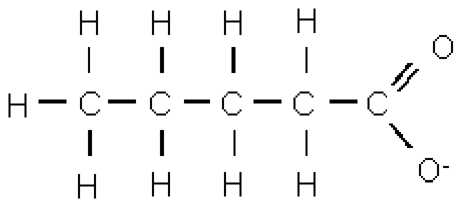
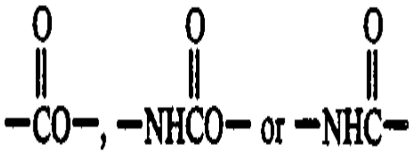


Figure 2.2: Bonding of Polar and Ionic Molecules (Hydrophilic)

The hydrophobic and hydrophilic groups must have a reactive group with which they can be reacted with the reactive group at the surface of the particles to be modified. The hydrophobic and/or hydrophilic groups are linked with the particle matrix through a –CO or –SiO bridge (Gruning & Holtschmidt, 1987).



$-\overset{\overset{O}{\|}}{C}O-,\ -NH\overset{\overset{O}{\|}}{C}O-$ or $-NH\overset{\overset{O}{\|}}{C}-$

Figure 2.3: Particles Matrix Bridge

2.3 UNMODIFIED AND MODIFIED SILICA

Silica (SiO_4) has a basic tetrahedral structure, where four oxygen atoms surround a central silicon atom (Jal et al., 2004). The SiO_4 stoichiometry of silica requires that each oxygen atom must be shared by silicon atoms in two tetrahedral. Because silicon atoms on the surface of natural, unmodified silicon dioxide are surrounded only by two, not four oxygen atoms, they are highly strained and react with water molecules present in the air to form silanol groups (Si-OH). The Si-OH groups present in the structure are the main source of hydrophilicity (water-attractive) because they promote the adsorption of water (Wagh & Ingale, 2002). The resultant surface of natural, unmodified silica contains both siloxane (O-Si-O) groups and silanol groups.

Silica is nano-structured materials with open foam having low density, high specific surface area and high porosity (Unob et al., 2007). These features lead to unique properties and due to excellent accessibility of the inner surface through open porous network, the most important feature of silica is the possibility to control its hydrophobicity (Štandeker et al., 2007). Silica exists in two varieties, amorphous and crystalline. Found most commonly in the crystalline state. In its amorphous state, silica does not have a regulat lattice pattern in the structure. In contrast, in its crystalline form, silica has a long range regular lattice pattern, characterized by tetrahedral configuration of atoms in the crystals.

The hydrophobicity of the silica can be achieved commonly by two methods. Silanization of a silica surface provide a basis for the transformation of the greater part of silanol groups (Si-OH) into hydrophobic trimethylsilyl groups, and thereby lowers the affinity of modified silicas to water. The second most commonly used method for producing hydrophobic silica is the chemical attachment of long-chain hydrocarbon radicals to their surfaces (Belyakova & Varvarin, 1999).

This surface modification does not affect the bulk properties of the silica but it does change the surface, and naturally accompanying the moisture absorption (or wettability) of the particle. Hexamethyldisilazane (HMDS), trimethylchlorosilane (TMCS) or various other organosilanes such as monoalkyl, dialkyl and trialkyl can be used as silation agent (Belyakova & Varvarin, 1999) (Kartal & Erkey, 2010) (Jal et al., 2004). The best treating agent as far as imparting superior hydrophobicity while maintaining oleophilicity is HMDS (Warrenchak & Phelan, 1991). The reaction occurred as below:

$$2\text{Si–OH} + (\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3 \longrightarrow 2\text{Si–O–Si}(\text{CH}_3)_3 + \text{NH}_3$$

Following modification, the silica surface become more hydrophobic, exhibiting enhance affinity to organic compound (Jesionowski & Krysztafkiewicz, 2002). The replacement of the Si-OH group by hydrolytically stable Si-R (R=CH_3) groups inhibits the adsorption of water and therefore results in hydrophobic silica that will be unaffected by the moisture (Wagh & Ingale, 2002). The present paper is devoted to study on the surface chemistry of silica modified with HMDS.

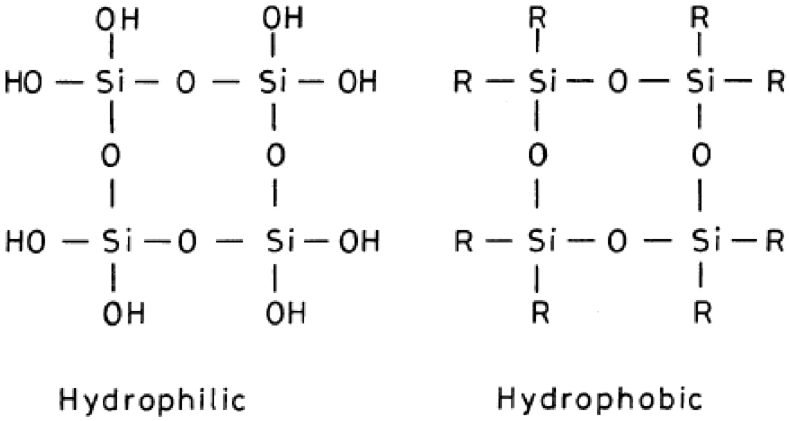


Figure 2.4: Schematic Diagram Showing Hydrophilic and Hydrophobic Silica

2.4 SYNTHESIS OF NANO SILICA PREPARED BY PRECIPITATION METHOD

There are several types of silica, such as fumed silica, precipitated silica, silica gel and colloidal silica, manufactured by different methods. For instance, precipitated silica is prepared by neutralizing a solution of sodium silicate with an sulphuric acid (liquid-liquid procedure) followed by drying of polysilicic acid (Jal et al., 2004).

$$Na_2SiO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2SiO_3$$
$$H_2SiO_3 \longrightarrow SiO_2 + H_2O$$

The silica particles were generated from the process comprises bringing an alkali metal silicate into contact with sulphuric acid in an aqueous solution. The preparation parameter such as the reaction time affect the final product physical properties, such as specific surface area, pore size, pore shape and particle morphology as well as chemical properties such as silanol group density.

The concentration of the sand in sodium hydroxide solution is depending on the reaction time. The reaction yield was calculated as the actual weight of precipitate produced, as a percentage of the theoretical quantity possible based on the amount of sand used (Wang et al., 1999).

The specific surface area of silica particles is very high and the aggregation rate decreased when prepared silica in the glycerol system. The resulting spherical silica particles with a very narrow particle size distribution are synthesized. The adsorption method using glycerol gave better results (Vacassy et al., 2000). Method of preparing silica nanoparticles from sand using chemical reaction comprises: removing impurities from the siliceous mudstone which is a raw material by a leaching reaction using sodium hydroxide. Further steps comprise performing heat treatment to remove a water constituent contained in the siliceous mudstone.

2.5 METHOD FOR PREPARATION OF NANO SILICA

One of the alternatives for synthesis of nano silica is extraction from rice husk ash. Rice husk ash (RHA) obtained after burning the rice husk is classified as an industrial waste. Rice husk (RH) consists of about 40% cellulose, 30% lignin group and 20% silica. By burning rice husk at temperature higher than 700°C crystalline silica is formed. The procedure of preparation the nano silica and treated silica (HRHA) is almost the same with using the siliceous sand (Amutha et al., 2010). It is suggested that rice husk ash is an alternative source of amorphous silica. The cost is supposed to be less but with equivalent properties (Amutha et al., 2010).

2.6 APPLICATIONS OF SILICA

Silica sand has a large number of industrial uses depending on their characteristics. Silica sand is the principal filtration medium used by the water industry to extract solid impurities from waste water. Water industries in Europe use millions of tones of filtration sands each year. Silica has played a continuous part in man's development and been one of the basic raw materials supporting the industrial revolution (Anonymous, 2010).

Silica in its finest form is also used as functional filler for paints, plastics, rubber, and silica sand is used in water filtration and agriculture. Other than that, silica is a widely use in silicon production, electronic industry, building materials and glass production (Anonymous, 2010).

CHAPTER 3

METHODOLOGY

3.1 PREPARED POWDER FORM OF SILICEOUS SAND

The siliceous sand which is silica mineral sources is grinding using grinder. As the result, powder form silica sand is getting with large surface area. The powder form silica sand is characterized using available equipments such as FTIR, XRD and SEM. The method of preparing silica nanoparticles from siliceous sand comprises several steps that will be discussed later.

3.2 SYNTHESIS OF NANO SILICA FROM SILICEOUS SAND

Nano silica is prepared from siliceous sand using a chemical reaction by precipitation method. First, sand is heated with 10M sodium hydroxide (Refer Appendix A for manual calculation). The reaction occurred is as follows:

$$\underset{\text{(Sand)}}{SiO_2} + \underset{\text{(Sodium Hydroxide)}}{2NaOH} \rightarrow \underset{\text{(Sodium Silicate)}}{Na_2SiO_3} + \underset{\text{(Water)}}{H_2O} + \underset{\text{(Solid)}}{\text{Impurities}}$$

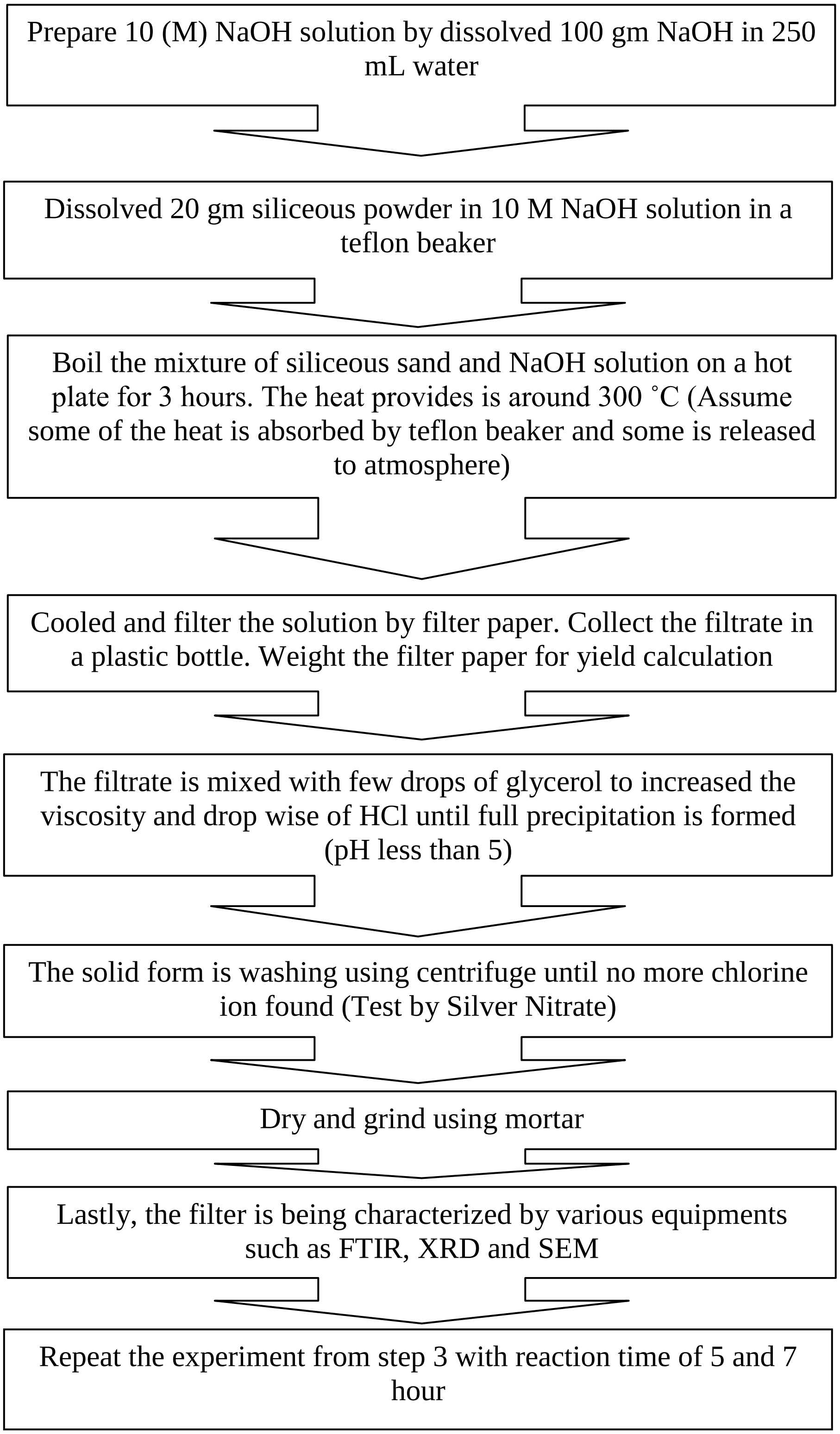
The reaction is taking place inside the Teflon beaker and is placed on the hot plate with temperature 300^0C. The sample of the solution is taken for each 30 minutes and few drops of hydrochloride acid are drop into the sample. The process is repeated until white precipitation can be observed. The reaction time has to be repeated for several times to observe the effect of reaction time with the yield. The reaction times are manipulated at 3, 5 and 7 hours (refer Appendix C1 for figure). The graph of yield versus reaction time is plotted to study the effect of reaction time on sodium silicate yield at constant temperature.

The solution is then filtered to separate the unreacted sand and sodium silicate (refer Appendix C2 and C3 for figure). The samples are then divided into two portions where one is without the glycerol and one with glycerol.

Glycerol is added into the solution to increase the viscosity and prevent agglomeration among particles. Next, the sodium silicate which is distillate is added with acidic acid until full white precipitation formed (refer Appendix C4 for figure). The process named precipitation method and being controlled by controlling the pH hydrochloric acid is added until the solution having pH less than 3. The reaction is as follows:

$$Na_2SiO_3 \quad + \quad 2HCl \quad \rightarrow \quad H_2SiO_3 + 2NaCl$$

All samples are then washed repeatedly in distilled water under identical conditions until no more chlorine found in the solution by using the centrifuge. The coloring of the sample after and before washing process is observed (refer Appendix C5 for figure). The centrifuge process continued for 20 min at 500 rpm for each batch. In the case of there is a white precipitation in the sample while adding the silver chloride, mean that the sample still contain the chloride ion (Cl^-). Water from H_2SiO_3 is removed by drying and follows by grounding so that amorphous silica is formed (refer Appendix C6 and C7). The silica then is characterized using FTIR, SEM and XRD to study their properties. Summary of steps is shown in diagram below:



Prepare 10 (M) NaOH solution by dissolved 100 gm NaOH in 250 mL water

Dissolved 20 gm siliceous powder in 10 M NaOH solution in a teflon beaker

Boil the mixture of siliceous sand and NaOH solution on a hot plate for 3 hours. The heat provides is around 300 ˚C (Assume some of the heat is absorbed by teflon beaker and some is released to atmosphere)

Cooled and filter the solution by filter paper. Collect the filtrate in a plastic bottle. Weight the filter paper for yield calculation

The filtrate is mixed with few drops of glycerol to increased the viscosity and drop wise of HCl until full precipitation is formed (pH less than 5)

The solid form is washing using centrifuge until no more chlorine ion found (Test by Silver Nitrate)

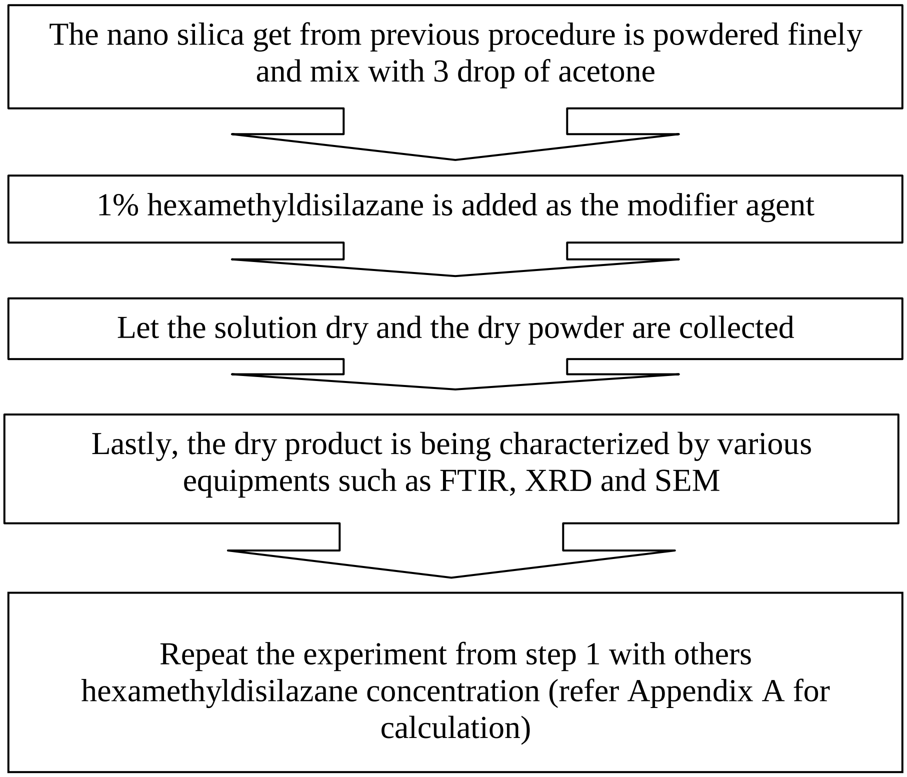
Dry and grind using mortar

Lastly, the filter is being characterized by various equipments such as FTIR, XRD and SEM

Repeat the experiment from step 3 with reaction time of 5 and 7 hour

3.3 NANO SILICA SURFACE MODIFICATION

The synthesis is then followed by the modification surface of the nano silica by the application of hexamethyldisilazane (HMDS). Theoretically, the process will result in nano silica which employs the hydrophobic characteristic. Acetone is added into the silica powder so that HMDS is well mixed. After the nano silica surface modification, it will then be characterized to know its properties (refer Appendix C8 for figure). The characterization process is done with some equipment available such as FTIR, XRD and SEM. Summary of steps is shown in diagram below:



3.4 CHEMICALS AND APPARATUS

3.4.1 Chemicals

All the chemicals used are listed in Table 3.1 below.

Table 3.1: Chemicals Used with Approximate Amount

Chemical	Chemical Formula	Approximate Amount
Solid sodium hydroxide	$NaOH$	100 gm
Hydrochloric acid	HCl	100 mL
Glycerol	$C_3H_5(0H)_3$	20 mL
Acetone	$(CH_3)_2CO$	20 mL
Hexamethyldisilazane,	$(CH_3)_3SiNHSi(CH_3)_3$	20 mL
Siliceous Sand	SiO_2	1000 gm

3.4.2 Equipments and Apparatus

Table 3.2 below shows the apparatus and equipments used for the experiment work.

Table 3.2: Apparatus and Equipments Used for the Experimental Work

Apparatus and Equipments	
Grinder	Hot plate
Teflon beaker	Glass beaker
Centrifuge	Plastic Bottles
Mortar and pestle	Portable pH meter
Oven	Filter paper
Magnetic stirrer	Spatula

3.5 CHARACTERIZATION

3.5.1 Fourier Transform Infra-Red (FTIR) Spectra

Infrared spectra of the catalyst samples were obtained using Perkin–Elmer Spectrum One spectrometer. FTIR spectra are useful for the identification of functional groups (such as CH_3–, NO_3-, –OH, C–O, etc.) present in the nano silica. Approximately 1 mg of each sample powder was grinded with 200mg of IR-grade KBr. Then, the sample was transferred into a diecast and pressed into pellet using a hand-press. The disc was later placed in a sample holder to be scanned by the instrument. The FTIR spectrum of the pellet, taken over a wave number range of $4000cm^{-1}$ - $400cm^{-1}$, was recorded as the percentage of transmittance (%T) versus wave number. The functional groups are identified by characteristic peaks in the spectrum.

3.5.2 X–Ray Diffractometer (XRD)

X-ray diffraction finds the active phase located on silica surface. Monochromatic x-rays are used to determine inter-planar spacing of unknown materials and determine the bulk chemical species of the sample. Powder-XRD (Bruker D8 Advance) was conducted on the catalysts with CuKα radiation of 40 kV, 40 mA; 2θ angles from 2° to 80° and scan speed of 4°/min in order to identify the type of species present. Anatase phase will be detected on the catalyst (the most active phase) for photocatalytic reaction. The XRD peaks are compared with standards in order to determine the species present in a sample.

3.5.3 Scanning Electron Microscope (SEM)

The morphologies of the SiO_2 were determined using Hitachi-4700 field emission microscope using an acceleration voltage of 10kV. SEM is a type of electron microscope that images the sample surface by scanning it with a high energy beam of electron. Samples were coated with Pt and placed on a stage specially made for SEM before the analysis and image taking. The settings used are:

EHT : 20.00kV
Magnificient : 100KX

CHAPTER 4

RESULT AND DISCUSSION

4.1 EFFECT OF REACTION TIME ON YIELD

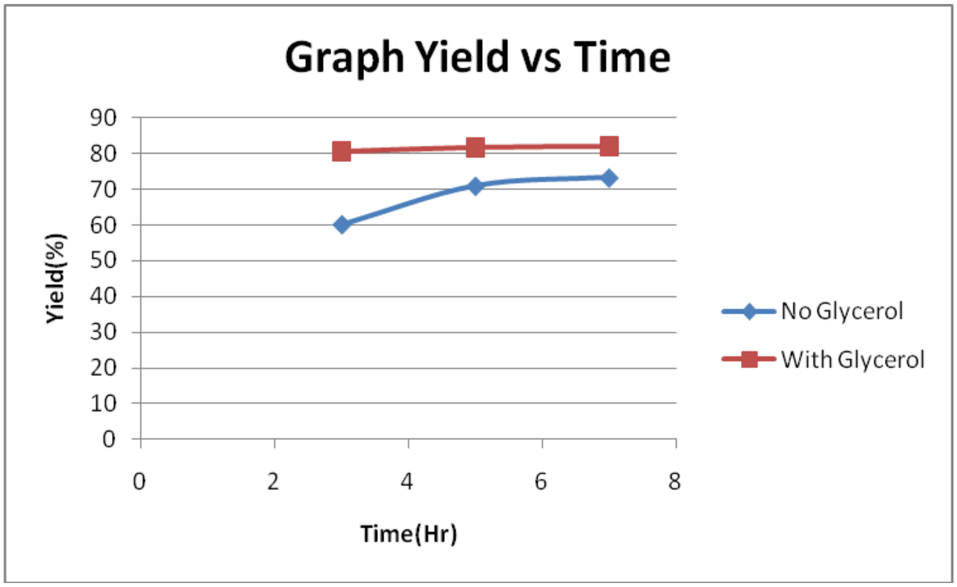


Figure 4.1: Graph Yield vs Reaction Time

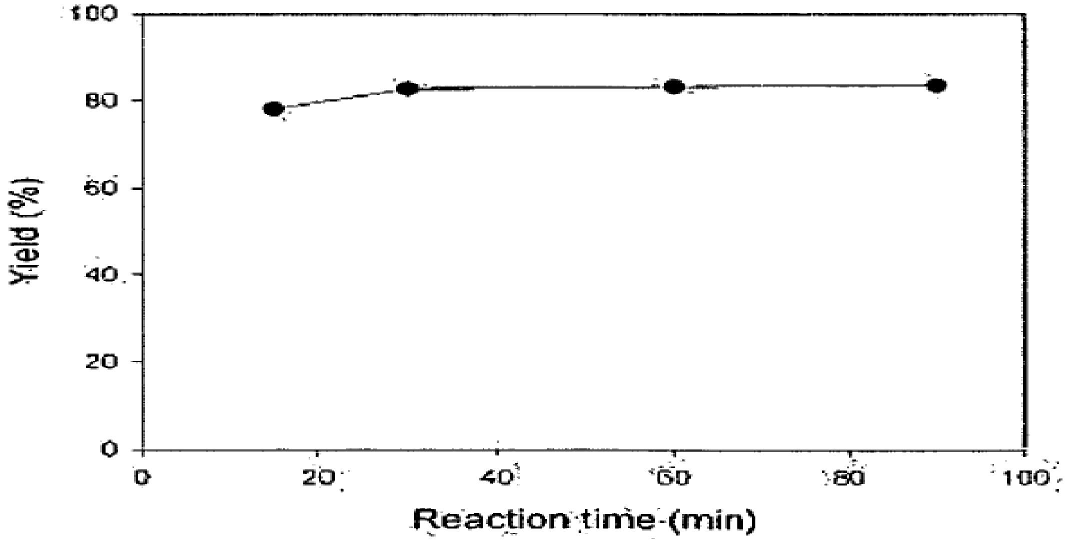


Figure 4.2: Graph Yield vs Reaction Time (Hee, 2008)

Figure 4.1 illustrates the yield of sodium silicate solution by solving the siliceous sand into a sodium hydroxide aqueous solution with different reaction time. The reaction temperature is fixed as 300 ˚C while the reaction time changes from 3 hr to 7 hr. The temperature 300 ˚C and reaction time from 3 hr to 7 hr is chosen because some of the heat is assumed to be released at the atmosphere. Moreover, some of the heat is absorbed by the teflon beaker. Two different solution is prepared where one without glycerol and another one with glycerol. The use of glycerol is to avoid agglomeration formation and hence control particle size of nano silica. The reaction take place is:

$$\underset{\text{(Sand)}}{SiO_2} + \underset{\text{(Sodium Hydroxide)}}{2NaOH} \rightarrow \underset{\text{(Sodium Silicate)}}{Na_2SiO_3} + \underset{\text{(Water)}}{H_2O} + \underset{\text{(Solid)}}{\text{Impurities}}$$

The extraction efficiency is increasing as the reaction time increase for both curves. However, the extraction efficiency is almost consistent at 82% for the solution with existence of glycerol. The yield of sodium silicate without presence of glycerol is increasing gradually and constant at 73% after 5 hr. It proves that the yield of sodium silicate solution is greater with the present of glycerol. The previous study manipulates the reaction time from 15 to 90 minutes under the condition that the reaction temperature is fixed at 100˚C. When the reaction time is more than 30 minutes, the extraction efficiency is consistent as 83%.

4.2 COMPONENTS ANALYSIS

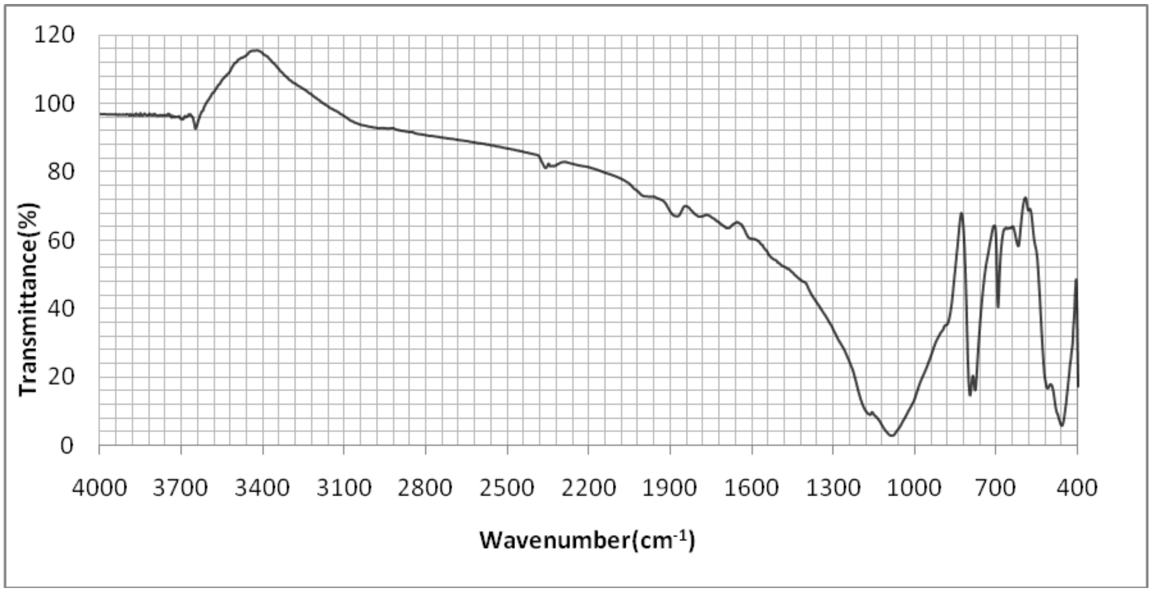


Figure 4.3: FTIR Spectra of Siliceous Sand

Based on Figure 4.3, there are absorption peaks at 1084 cm^{-1}, 797 cm^{-1} and 460 cm^{-1} in the FTIR spectra curves which demonstrate to the vibrations of Si-O-Si groups in the siliceous sand. This ensures the existence of silica component in the sand. In addition, three absorption peaks at 1599 cm^{-1}, 1877 cm^{-1} and 694 cm^{-1} have appeared which are ascribed to the water, C-N and R-Cl vibration, respectively from Figure 4.3.

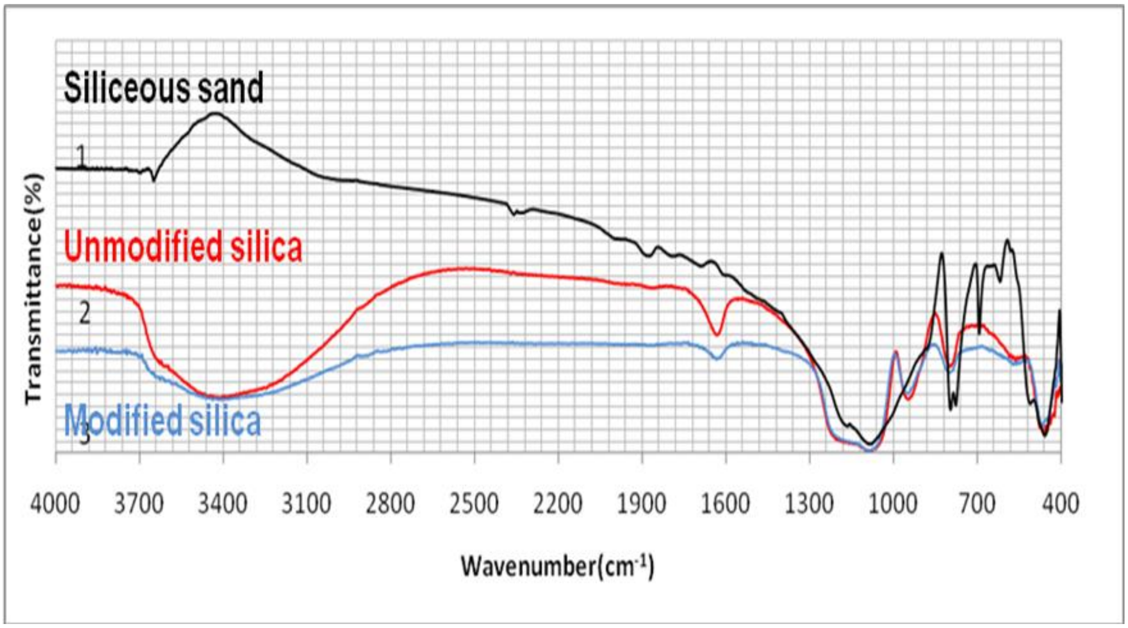


Figure 4.4: FTIR Spectra of the 1) Siliceous sand 2) Nano Silica Prepared Without HMDS and 3) Modified Nano Slica with HMDS

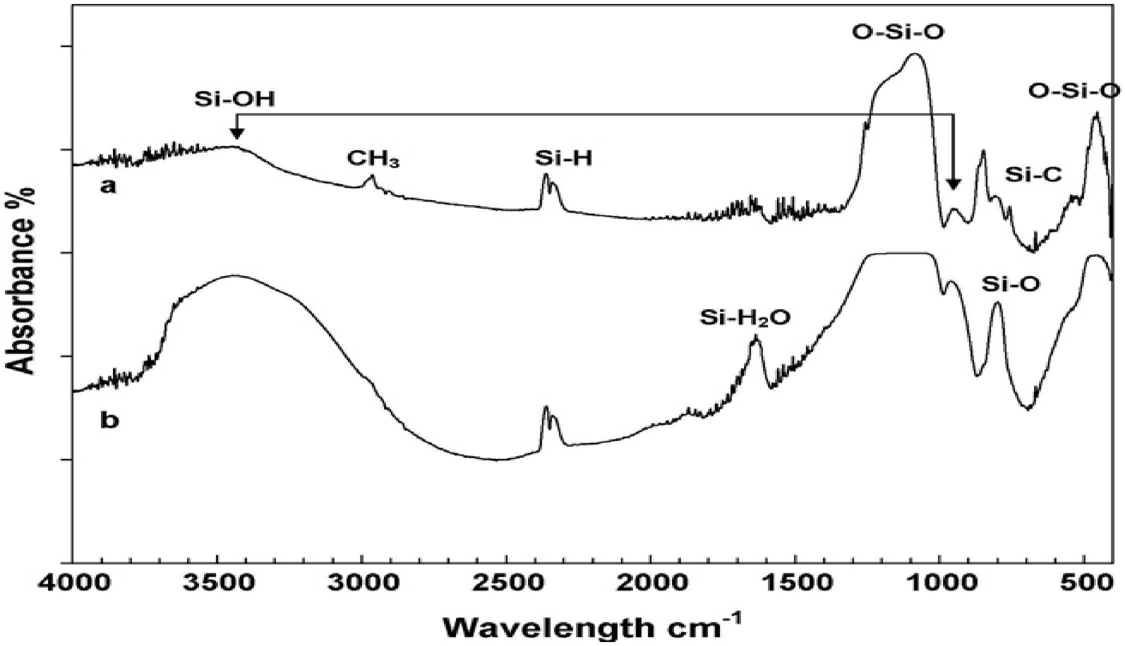


Figure 4.5: FTIR of Treated (above) and the Untreated Silica (below) (Kartal & Erkey, 2010)

FTIR spectra of unmodified SiO_2 particles and those modified with hexamethyldisilazane (HMDS) surfactant are presented in Figure 4.4. Compared to curve 1, both curve 2 and 3 having no more chlorine since the chlorine is removed by washing process during synthesis. This is proven by smooth curve at 694 cm^{-1}. It is seen that the relative intensities of the peaks around 1100 cm^{-1} for siliceous sand are higher than those for unmodified and modified nona-silica. The absorption at 1100 cm^{-1} can be ascribed to the characteristic Si–O–Si asymmetric stretching vibration.

A new absorption peaks at 1632cm^{-1} in curves 2 and 3 of Figure 4.4 may be attributed to the vibration of C-N. In both spectra, peak associated with the silicon dioxide network (Si-O-Si) and the alkyl groups (CH_3) appeared at 1082 cm^{-1}. The addition of silica nanoparticles also broadens the peak at 3400 cm^{-1} in curve 2 and 3, which is the characteristic band of O–H (Si–OH) groups. The result obviously shown that the modified silica intensities of Si-OH around both 3400 cm-1 and 1100 cm-1 are reducing. While a weak -OH as well as water associated peaks can be seen at 3650 cm^{-1} and 1690 cm^{-1}, respectively, in the curve 1. Table 4.1 summarize the components exists in silica samples.

Figure 4.5 present the infrared transmittance spectra for the silica based on previous study. The comparison of the spectra of the treated and the untreated samples clearly indicates that the silica were modified since the intensities of the broad Si–OH band around 3500cm^{-1} and the other Si–OH peak around 1000cm^{-1} were reduced. In addition, the presence of sharp Si–CH_3 peak around 2900cm^{-1} in the treated samples indicates that the reaction of HMDS with silanol groups has occurred (Kartal & Erkey, 2010). However, in curve 3 of Figure 4.4, the Si–CH_3 peak can be improve by increase the concentration of HMDS used to 3% or 5%.

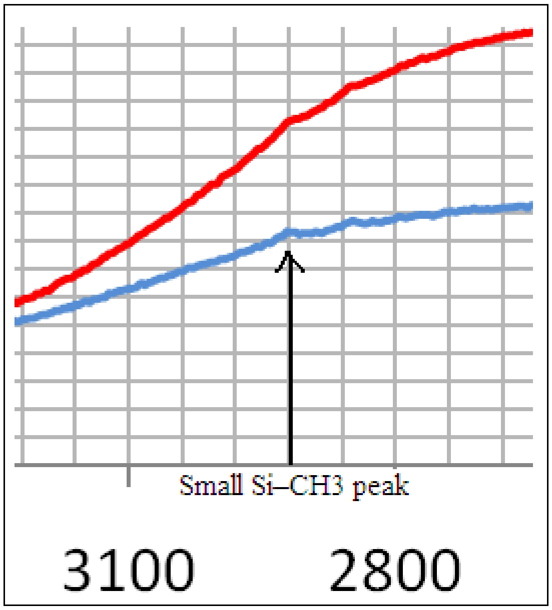


Figure 4.6: FTIR Indicating Small Si–CH_3 Peak

Table 4.1: FTIR Frequency with Position Assignment (Jal et al., 2004)

FTIR Frequency (cm^{-1})	Position Assignment
462	Si-O bond rocking
800	OH Bending (silanol)
980-970	Si-OH bond
1102	Asymmentric Si-O-Si
1630	O-H bending (molecular water)
3000-4000	O-H adsorbed water
2909	Si-CH_3

4.3 PHASE ANALYSIS

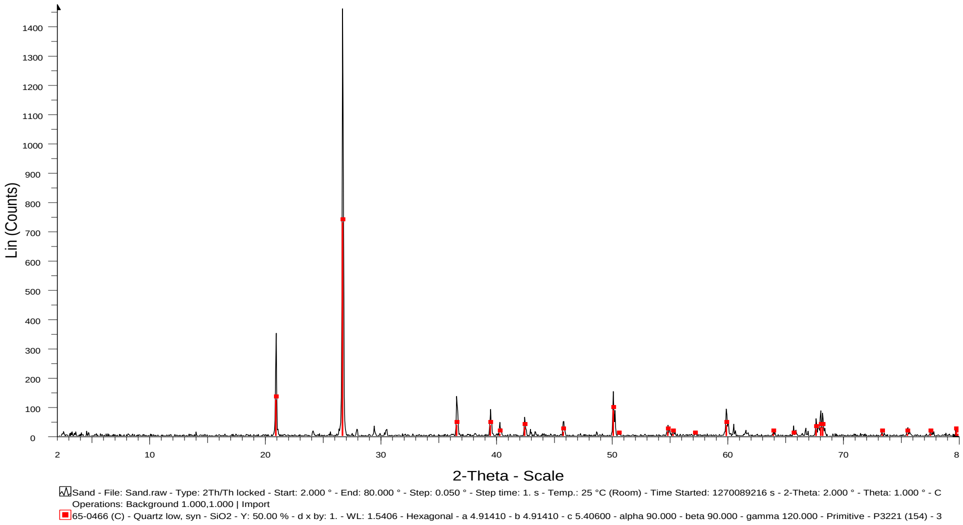


Figure 4.7: XRD Pattern for Siliceous Sand

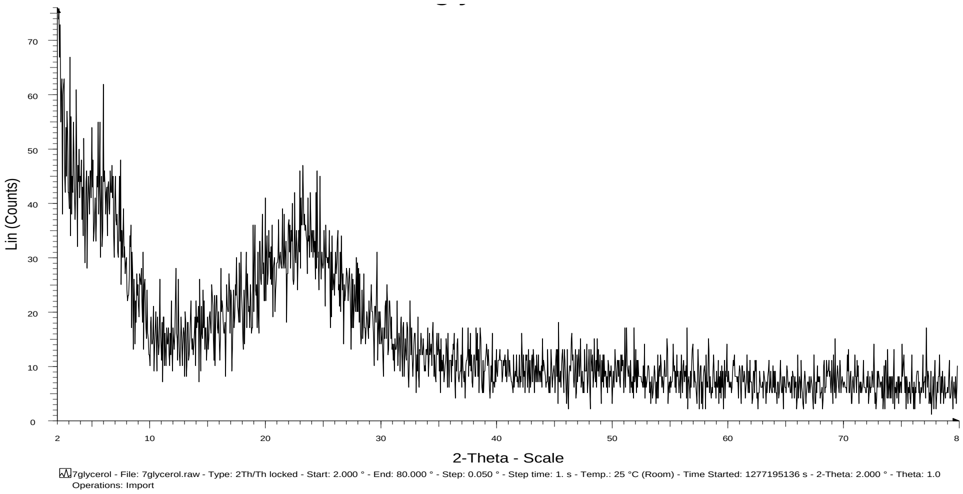


Figure 4.8: XRD Pattern for Nano Silica

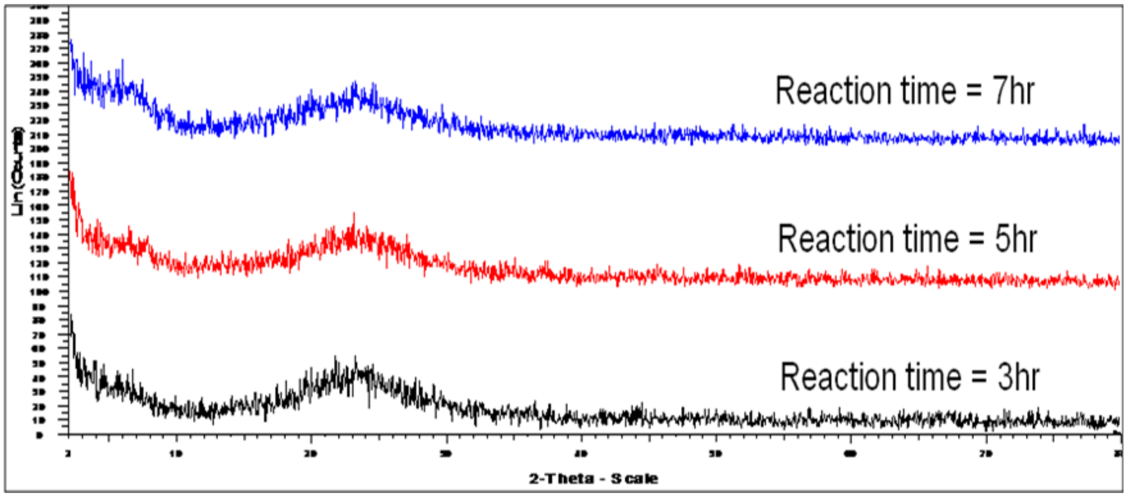


Figure 4.9: Comparison of XRD Analysis at Different Reaction Time

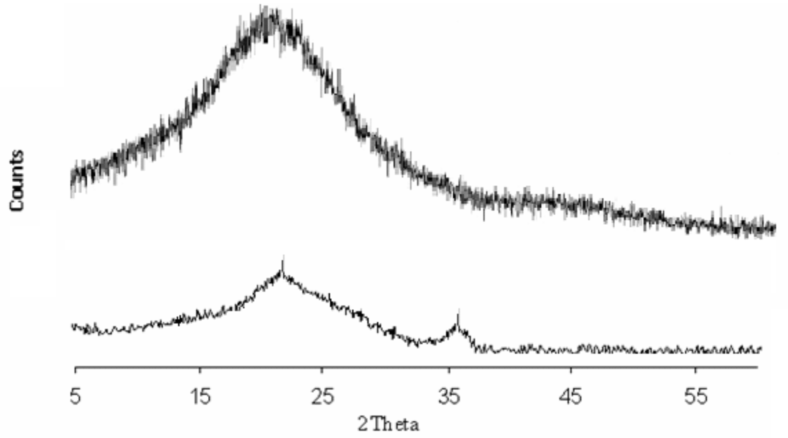


Figure 4.10: XRD Spectra of Rice Husk (below) and Nano Silica (above) (Amutha et al., 2010)

Based on Figure 4.7, siliceous sand is in crystalline order. It was proposed that the crystal structure of siliceous sand is hexagonal structure as the axes are $a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$ where $a = 4.9141$, $b = 4.9141$ and $c = 5.4060$. The diffractogram of nano silica is observed with a hump in the 2θ ranging from 15º to 40º indicating disordered structure, due to silica particles. While the diffractogram of nano silica is observed having the strong peak centered at 2θ angle of 22º indicated the amorphous nature of silica. Based on Figure 4.9, the peaks pattern are all the same. These indicate that the reaction time will not change the mechanical properties of nano silica. The phase of all the synthesis silica is in amorphous phase. The powder X-ray diffraction patterns of rice husk and nano silica are shown in Figure 4.10. From the mineralogical point of view is mainly constituted with amorphous silica with low crystalline. The diffractogram of is observed with a hump in the 2θ ranging from 15º to 40º indicating disordered structure, due to amorphous silica particles. The XRD pattern of nano silica with strong broad peak centered at 2θ angle of 22º confirms the amorphous nature of silica.

4.4 PARTICLE SIZE AND MORPHOLOGY ANALYSIS

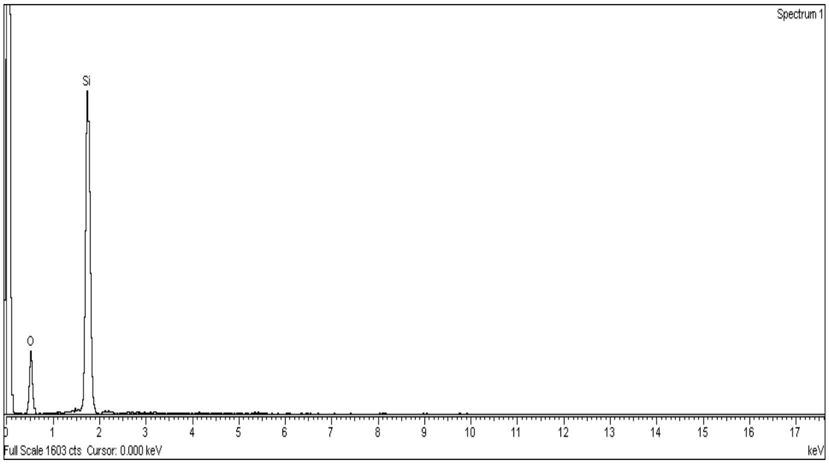
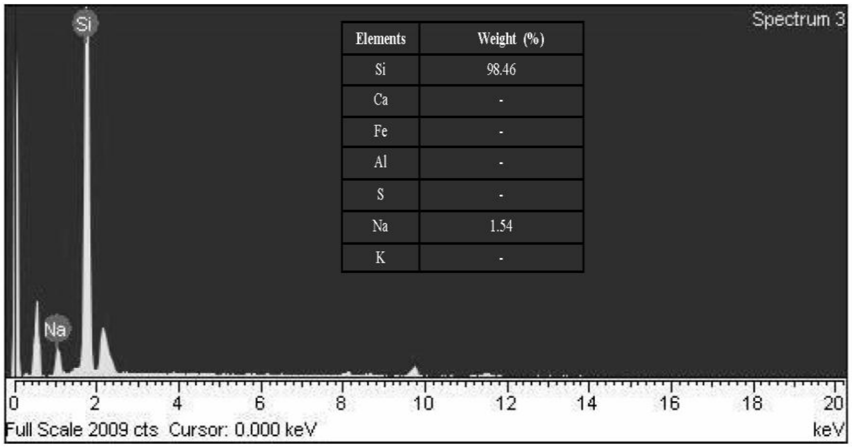


Figure 4.11: EDS Plot of Siliceous Sand

Table 4.2: Element Exist in Siliceous Sand

Element	Weight (%)	Atomic (%)
O	53.50	66.88
Si	46.50	33.12



Elements	Weight (%)
Si	98.46
Ca	-
Fe	-
Al	-
S	-
Na	1.54
K	-

Figure 4.12: EDS of Nano Silica from Rice Husk (Amutha et al., 2010)

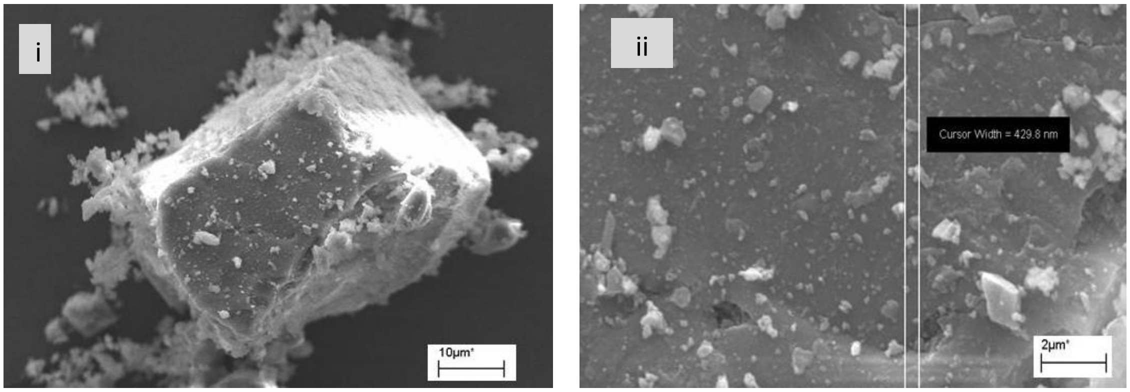


Figure 4.13: SEM Micrographs of Siliceous Sand: (i) 1000 magnified (ii) 5000 magnified

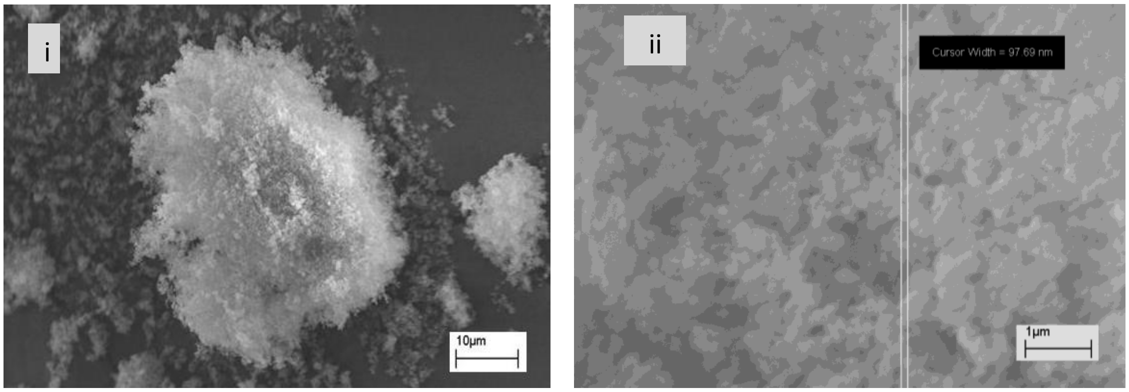


Figure 4.14 SEM micrographs of Unmodified Silica without Glycerol: (i) 1000 magnified (ii) 5000 magnified

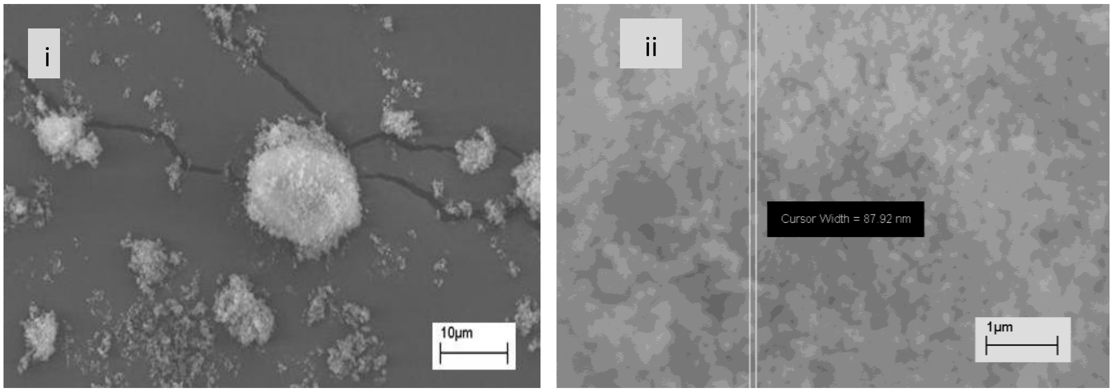


Figure 4.15: SEM micrographs of Modified Silica with HMDS and with Glycerol: (i) 1000 magnified (ii) 5000 magnified

The EDS results are shown in Figure 4.11 and Table 4.2 above. EDS analysis show the siliceous sand contains 46.50% Si and 53.50% of O. The analysis confirms the presence of Silicon (Si) and Oxygen (O) compounds and thus prove the capability of siliceous sand as the adsorbent. Same as sand, EDS profile of nano silica from rice husk particle in Figure 4.12 evidence predominantly with element Si.

The SEM micrographs of siliceous sand are shown in Figure 4.13. While precipitated silica with unmodified and modified SiO_2 particles with HMDS are presented in Figures 4.14 and 4.15, respectively. It indicates that the shapes of the siliceous sand particles are uniformly crystal with flat surface area. The particle mean size of the sand is larger than that of the precipitated silica. The average size is measured around 430nm for siliceous sand and reduced to 98nm for the unmodified silica and around 88nm for the modified ones.

However, based on Figure 4.14 and 4.15, the particle size and surface area of the precipitated silica obtained is in an indefinite or spherical shape. The microscopic observation reveals that the particles comprise of amorphous silica particles with extremely fine particles. As shown in Figure 4.15 (i), the HMDS modified silica nanoparticles were well distributed, with small particle sizes (88nm).

The silica modified with glycerol produced less agglomeration particles (Figure 4.15i). Agglomeration influences the particle size and morphology of the samples. For the best adsorbents, fine particles are to be produced with fewer agglomerates.

Figure 4.16 shows the SEM picture of rice husk and nano silica synthesis from rice husk. Same as sand, the rice husk particles mainly in irregular morphology. Based on Amutha, 2010, the average particles size of rice husk is 5µm while the particle size of the nano silica synthesis from rice husk is about 70-80 nm in agglomeration from with spherical shape (Figure 4.16).

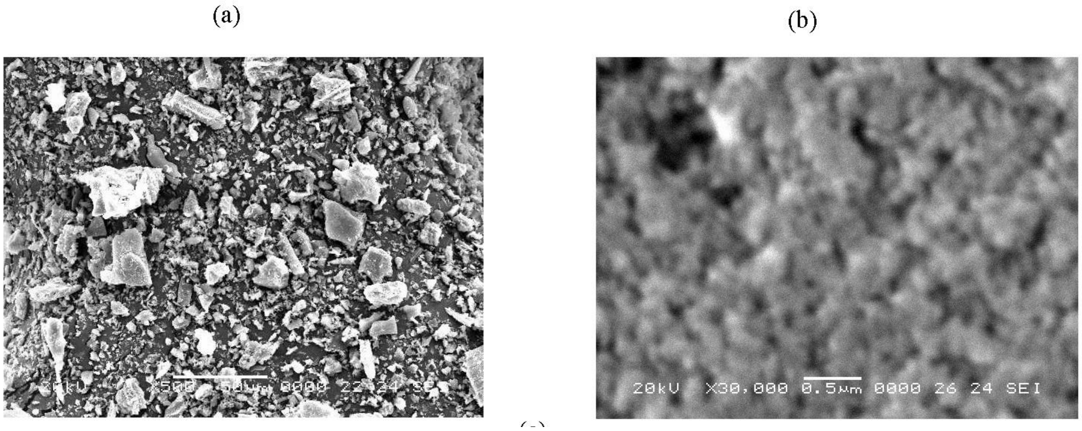


Figure 4.16: SEM Picture of Rice Husk and Nano Silica (Amutha et al., 2010)

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

A number of modification techniques have been developed in recent years to improve the adsorbents activity for emulsion adsorption. Silica have been proven on the ability to be a good adsorbent with properties of high specific area, high porosity and easy for modification. Presently, the silica adsorbent is obtained from local siliceous sand since it is abundant waste and less expensive compared to chemical reaction.

Siliceous sand can be used to synthesis the modified nano silica because it is proven by FTIR, XRD and SEM testing that absence of silica components inside the sample. The experiment shows the silica yield increase with reaction time. Presence of glycerol reduces the interactions between particles and these agglomerates can be broken down more easily. The synthesis of nano silica by precipitation method produced nanoparticles that are fined and spherical shape with amorphous phase. Based on the study using FTIR, the hydrophobicity of silica nanoparticles can be improved by modification with hexamethyldisilazine.

In principle, all these properties make silica to be expected to possess a good adsorbent. It is anticipated that the low cost, environmentally friendly will play an important role in the oil and gas industry and contribute much to the coming environmental problems.

5.2 RECOMMENDATION

Further studies are recommended based on the current result especially from current studies. Further study on hydrophobicity test of nano silica by using another hydrophobic substance can be done. Moreover, use rise husk instead of using the local siliceous sand as the raw material for synthesis the nano silica. The process of preparing nano silica from rice husk is less complex compared by using the local sand. However, more literature review needs to be done continuously in order to get the best result.

CHAPTER 6

REFERENCES

1. Ahn, S. H., Kim, S. H.& Lee, S. G. (2004). Surface-modified silica nanoparticle-reinforced poly(ethylene 2,6-naphthalate). *Journal of Applied Polymer Science*, *94*(2), 812-818.
2. Amutha, K., Ravibaskar, R.& Sivakumar, G. (2010). Extraction, synthesis and characterization of nanosilica from rice husk ash. *Journal of Nanotechnology and Applications*, *4*(1), 61-66.
3. Anonymous (2010). *Fact on silica.* Retrieved August 25, 2010, from http://www.ima-eu.org/fileadmin/eurosil/Silica05.pdf.
4. Belyakova, L. A.& Varvarin, A. M. (1999). Surfaces properties of silica gels modified with hydrophobic groups. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *154*(3), 285-294.
5. Peterson et al. (2003).Long Term Ecosystem Response to the Exxon Valdez Oil Spill. *Journal of Science, 302*(5653), 2082-2086.
6. Choma, J., Kloske, M.& Jaroniec, M. (2003). An improved methodology for adsorption characterization of unmodified and modified silica gels. *Journal of Colloid and Interface Science, 266*(1), 168-174.
7. Gruning,B.&Holtschmidt, U. (1987).United State Patent No 4715986. Washington, DC: US Patent and Trademark Office.

8. Jal, P. K., Patel, S.& Mishra, B. K. (2004). Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions. *Journal of Surface Science*, *62*(5), 1005-1028.
9. Jal, P. K., Sudarshan, M., Saha, A., Patel, S.& Mishra, B. K. (2004). Synthesis and characterization of nanosilica prepared by precipitation method. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 240*(1-3), 173-178.
10. Jesionowski, T.& Krysztafkiewicz, A. (2002). Preparation of the hydrophilic/hydrophobic silica particles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 207*(1-3), 49-58.
11. Jin, Y., Li, A., Hazelton, S. G., Liang, S., John, C. L., Selid, P. D. et al. (2009). Amorphous silica nanohybrids: Synthesis, properties and applications. *Coordination Chemistry Reviews*, *253*(23-24), 2998-3014.
12. Kartal, A. M.& Erkey, C. (2010). Surface modification of silica aerogels by hexamethyldisilazane–carbon dioxide mixtures and their phase behavior. *The Journal of Supercritical Fluids*, *53*(1-3), 115-120.
13. Lerner, K. L.& Lerner, W. B. (2006). *Hydrophobic and hydrophilic.* Retrieved August 25, 2010, from http://www.enotes.com/microbiology-encyclopedia/hydrophobic-hydrophilic.
14. Li, L., Quinlivan, P. A.& Knappe, D. R. (2002). Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution. *Carbon Journal*, *40*(12), 2085-2100.
15. Liou, T. (2004). Preparation and characterization of nano-structured silica from rice husk. *Materials Science and Engineering*, *364*(2), 313-323.

16. Liu, H., Sha, W., Cooper, A. T.& Fan, M. (2009). Preparation and characterization of a novel silica aerogel as adsorbent for toxic organic compounds. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 347*(3), 38-44.
17. Nora, S.& Mamadou, S. D. (2005). Nanomaterials and water purification: Opportunities and challenges. *Journal of Nanoparticle Research,* (7), 331-342.
18. Štandeker, S., Novak, Z.& Knez, Ž. (2007). Adsorption of toxic organic compounds from water with hydrophobic silica aerogels. *Journal of Colloid and Interface Science, 310*(2), 362-368.
19. Tom, B.& Deborah Z. (2010). *Mexico Disaster gulf is not the first disaster to the BP*. Retrieved September 18, 2010, from http://www.commercialdivingmagazine.com/news/mexico-disaster-gulf-is-not-the-first-disaster-to-the-bp/.
20. Unob, F., Wongsiri, B., Phaeon, N., Puanngam, M.& Shiowatana, J. (2007). Reuse of waste silica as adsorbent for metal removal by iron oxide modification. *Journal of Hazardous Materials, 142*(2), 455-462.
21. Vacassy, R., Flatt, R. J., Hofmann, H., Choi, K. S.& Singh, R. K. (2000). Synthesis of microporous silica spheres. *Journal of Colloid and Interface Science, 227*(2), 302-315.
22. Warrenchak,J. F.&Phelan, E. F. (1991).United State Patent No 5037557. Washington, DC: US Patent and Trademark Office.

23. Wagh, P. B.& Ingale, S. V. (2002). Comparison of some physico-chemical properties of hydrophilic and hydrophobic silica aerogels. *Ceramics Journal, 28*(1), 43-50.
24. Wang, L., Wang, Z., Zhao, J., Yuan, Z., Yang, H.& Zhao, M. (1999). Preparation of mesoporous silica by co-precipitation in the presence of non-ionic surfactant. *Materials Chemistry and Physics, 59*(2), 171-174.

APPENDICES

APPENDIX A

MANUAL CALCULATION

1) Manual molar calculation for sodium silicate solution preparation

$n = MV/ 1000$

$n = m/ MW$

where n = number of mole
M = Molarity
V = Volume of the water
m = mass of the solute
MW = Molecular weight of the solute

To prepared 10(M) NaOH solution,

$$n = 100\text{g} / 40 \text{ g-mol} = 2.5 \text{ mol}$$

$$V = \frac{n * 1000}{M} = \frac{2.5 * 1000}{10} = 250 \text{ mL}$$

2) Volume hexamethyldisilazane for 1% wg/wg

$$1\% \text{ wg/wg} = \frac{1 \text{ g HMDS}}{100 \text{ g silica}} = \frac{0.00305 \text{ g HMDS}}{0.3050 \text{ g silica}}$$

$$\text{Volume of HMDS, } V = \frac{m}{\rho}$$

$$= \frac{0.00305\ \text{g}}{0.774\ \text{g/mL}}$$

$$= 0.00394\ \text{mL}$$

$$= 3.94\ \mu\text{L}$$

APPENDIX B

GANTT CHART (1ST SEMESTER)

No.	Activity	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Release of FYP Topics for selection	🟥														
2	Briefing to students on " FYP Research Background " & Distribution of FYP Guideline	🟥														
3	Submission of FYP Topic Selection	🟥														
4	Release of FYP Topic Assigned		🟥													
5	FYP Seminar Series commence "Research Methodology" by Dr Suriati		🟥													
6	Submission of FYP Proposal		🟥													
7	Preliminary Research work		🟥	🟥	🟥											
8	Briefing on "Library Facilities & How to access Journals"				🟥											
9	Project Work continues - Literature review findings - Working experiment in lab					🟥	🟥	🟥								
10	Submission of Progress Report									🟥						
11	Seminar										🟥					
12	Experimental work					🟥	🟥	🟥		🟥	🟥	🟥	🟥	🟥	🟥	🟥
13	Submission on Final Interim Report															🟥
14	Final Oral Presentation															🟥

GANTT CHART (2nd SEMESTER)

No.	**Activity**	**1**	**2**	**3**	**4**	**5**	**6**		**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
1	First briefing and safety briefing by Lab Technician		🟥																	
2	Meeting with Dr Murugesan relating to the project work		🟥																	
3	Classes on Report Writing Technique given by Dr. Khalik			🟥	🟥	🟥	🟥		🟥	🟥	🟥	🟥	🟥							
4	Submission of Progress Report 1					🟥														
5	Experimental work		🟥	🟥	🟥	🟥	🟥		🟥	🟥	🟥									
6	Poster Exhibition											🟥								
7	Submission of Progress Report 2												🟥							
8	Engineering Design Exhibition (EDX)													🟥	🟥					
9	Submission of Dissertation														🟥					
10	Final Oral Presentation																	🟥	🟥	
11	Submission of hardbound copies																			🟥

APPENDIX C

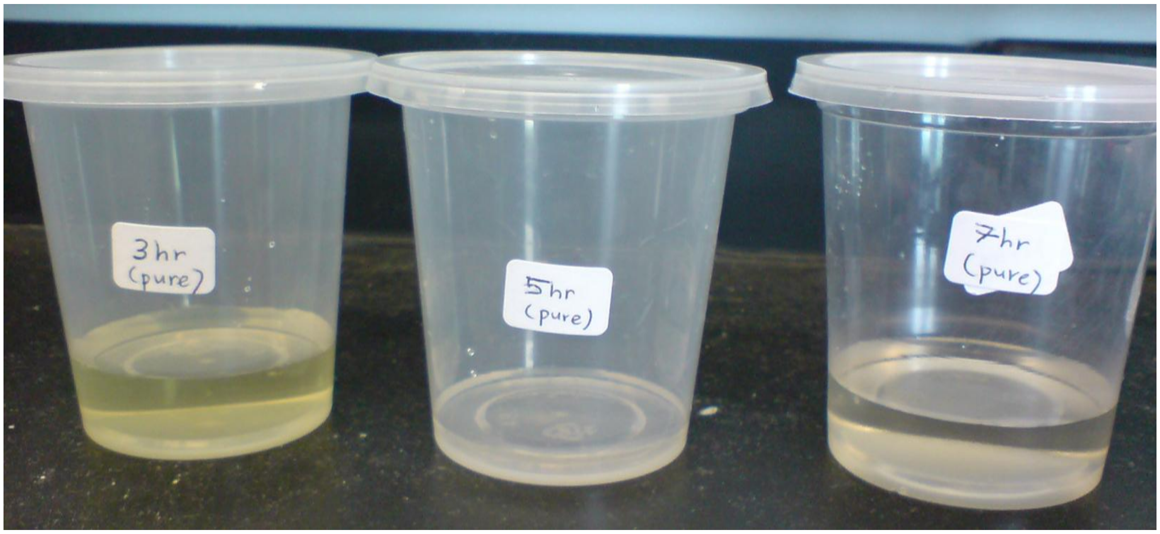


Figure C1: Sample Collected at Different Reaction Time

Figure C2: Sodium Silicate Filtration

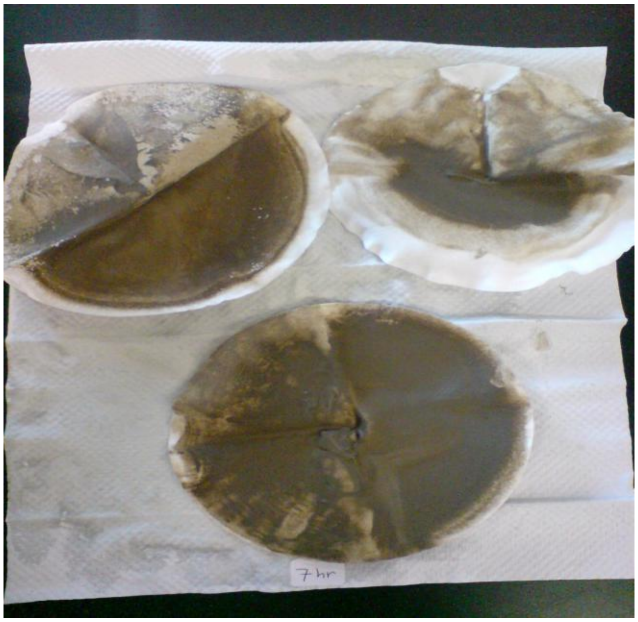


Figure C3: Unreacted Sand

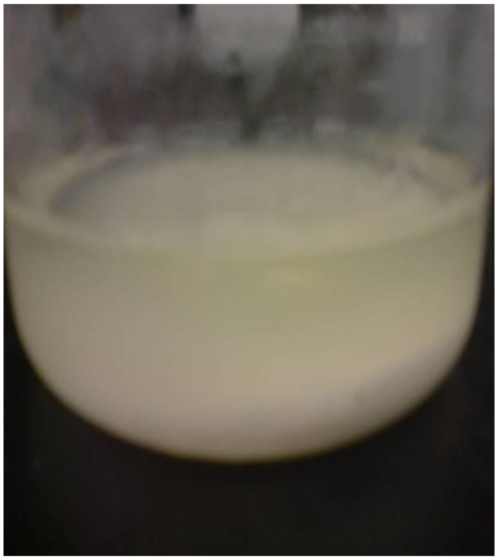


Figure C4: White Precipitation Formed for Reaction of HCl with Sodium Silicate

Figure C5: Sample of Sodium Silicate for Reaction Time 3hr: a) Before washing (left) and b) After washing (right)

Figure C6: Removing Water by Drying Process

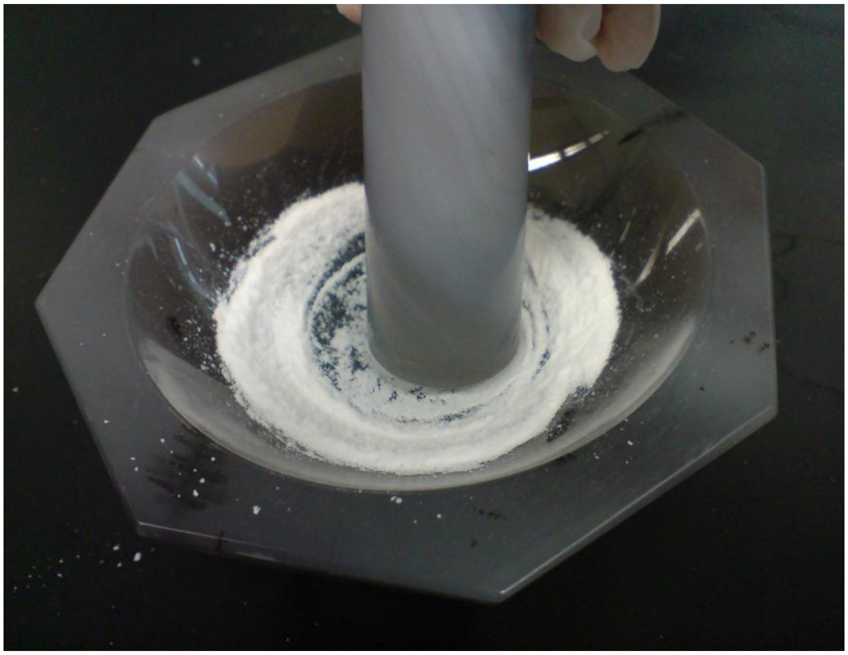


Figure C7: Grounding Process to Form fine Nano silica

Figure C8: Sample Prepared for Characterization Process