SYNTHESIS OF AMORPHOUS SILICA FROM SUGAR CANE LEAF BY CHEMICAL EXTRACTION METHOD

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Thesis submitted in fullfilment of the requirements
for the award of the degree of
Bachelor of Engineering in Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
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JANUARI 2012

ABSTRACT

Amorphous silica is the chemical compound that also known as silicon dioxide with the chemical formula SiO_2. Amorphous silica is the demand raw material nowadays by the chemical industry as it is widely used in the production of resin, optical beads, glass, porcelain and in the semiconductor circuit. Most of the amorphous silica previously were produce from rice husk ash due to its low cost and is environmentally friendly. This research was conducted to find an alternative way and optimum condition to produce amorphous silica from sugar cane leaves ash by chemical extraction method. This is due to its low cost and can be one of the effective ways to dispose agricultural waste. The scope of this research are to study the effect of extraction temperature used during extraction process, the effect of extraction time and the effect of different solvent used to the yield of amorphous silica produced. This research was conducted by using pretreatment method of the sugar cane leaves ash followed by soxhlet extraction method. Based on the results obtained and analysis, it was confirmed that sugar cane leaves is one of the sources to produce amorphous silica and the optimum condition to produce amorphous silica is at high temperature of extraction which is at 80°C, and 8 hours time of extraction and by using methanol as the extraction solvent. The silica obtained from the extraction process was characterized by using Fourier Transform Infrared Spectroscopy (FTIR). As a conclusion, it was confirm that sugar cane leaves contain SiO_2 compound based on the wavelength analysis obtained from FT-IR.

ABSTRAK

Silika amorfus adalah sebatian kimia yang juga dikenali sebagai silikon dioksida dengan formula kimia SiO_2. Silika amorfus mempunyai permintaan yang tinggi sekarang ini terutamanya oleh industri kimia kerana ia digunakan secara meluas dalam pengeluaran resin, manik optik, kaca, porselin dan dalam litar semikonduktor.Kebanyakan silika amorfus sebelum ini telah dihasilkan daripada abu sekam padi disebabkan oleh kosnya yang rendah dan mesra alam. Kebanyakan silika amorfus dihasilkan dari abu sekam padi sebelum ini. Melalui kajian ini kaedah alternatif dan kondisi optimum untuk menghasilkan silika amorfus dari daun tebu akan dikaji dengan menggunakan kaedah pengekstrakan kimia. Ini adalah disebabkan oleh kosnya yang rendah dan boleh menjadi salah satu cara yang berkesan untuk melupuskan sisa pertanian seperti daun tebu. Kajian ini akan menganalisa kesan suhu yang digunakan semasa proses pengekstrakan, kesan masa pengekstrakan untuk menghasilkan silika amorfus dan kesan menggunakan pelarut yang berbeza terhadap penghasilan silika amorpfus. Kajian ini telah dijalankan dengan menggunakan kaedah pra-rawatan terhadap abu daun tebu diikuti dengan pengekstrakkan dengan menggunakan pengekstrak soxhlet. Hasil dari kajian mendapati, keadaan optimum untuk menghasilkan silika amorfus adalah pada suhu pengeluaran yang lebih tinggi iaitu 80°C, menggunakan 8 jam masa pengekstrakkan dan menggunakan metanol sebagai pelarut organik . Silika yang diperolehi daripada proses pengekstrakan telah dianalisa dengan menggunakan Jelmaan Fourier Inframerah Spektroskopi (FTIR). Kesimpulannya, daun tebu telah terbukti mempunyai kandungan SiO_2 hasil dari analisis panjang gelombang yang diperolehi melalui FT-IR.

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LIST OF SYMBOLS

°C	Degree celcius
m^2	Square meter
%	Percentage
cm^{-1}	Per Centimeter

LIST OF ABBREVIATIONS

FAO	Food and Agriculture Organization
RHA	Rice Husk Ash
ICP-AES	Inductively Coupled Plasma-Atomic Electron Spestrometry
FT-IR	Fourier Transform Infrared Spectroscopy
2AP	2-acetyl-1-pyrroline

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

The amorphous silica is also known as silicon dioxide. The chemical formula for amorphous silica is SiO_2. The CAS number for amorphous silica is 7631-86-9 with molecular weight of 60.08 g/mol. The density of silicon dioxide is 2.648 g/m^3. Usually the amorphous silica is manufacture in several forms such as fused quartz, crystal and fumed silica (Kingsley, 2010).

Amorphous silica is the material that is widely used in various type of industry. For instance, in the chemical industry, the amorphous silica is used as the intermediate product to produce the catalyst, resin, optical beads, porcelain, glass and other chemical related products (Eduardo, 2009). This amorphous silica is also used as the component of semiconductor circuit to isolate different conducting regions. This is due to its mechanical resistance and high dielectric strength (Eduardo, 2009).

Amorphous silica is produced by the acidification of solution of sodium silicate to produce the gelatinous precipitate. There are several sources of amorphous silica. Some of the silica naturally forms in food such as in green vegetables, fruits, nuts and whole grains. The silicon dioxide is use as anti-caking agent in food (Food Additives and Ingredient Association, 2008).

1.2 PROBLEM STATEMENT

Most of the previous researches were using rice husk ash as their raw material to produce the amorphous silica. Silica produce from rice husk can be an alternative way to solve the disposal problem faced by rice milling industry. According to Dongmin et al., (2010), the rice husk is abundantly available in the countries that major in paddy producing. Since the disposal activities of rice husk could contribute to water and air pollution, the researcher find an alternative way on how to treat the rice husk by producing the amorphous silica from the rice husk.

The same problem goes to the sugar cane leaf. This is because most of the Asian countries producing sugar from sugar cane. The sugar industries only used the sugar cane. The sugar cane leaf becomes the major waste in the sugar producing industries and need to be disposed properly. Most of the sugar cane leaves was disposed by open burning system and this activities could contribute air pollution and effect human health (Rajeev and Rajvanshi, 1997). Otherwise, improper treatment of the cane leaf also could be major environmental problems.

For the past few years, the amorphous silica was produced using various types of material and also various methods. For instance, the previous researcher produces amorphous silica from rice husk by using sol-gel method (Junqi et al., 2011). The method used to dispose the sugar cane leaf actually requires high cost and also can contribute to air pollution (Kingsley, 2010). This research, would like to enhance the production of amorphous silica from sugar cane leaf by using pretreatment followed by chemical extraction method. Although, these methods already used by some of the existing researcher to produce amorphous silica, but this research studied different parameters that will affect the production of amorphous silica from sugar cane leaf by using chemical extraction method.

Besides that, sugar cane leaf is one of the raw material sources that is available in Malaysia and sugar cane is one of the plant that most suitable and easy to grow in the Asian climate especially in Malaysia. So, the cost to commercialize amorphous silica from sugar cane leaf source is inexpensive and feasible. Moreover, the method that will be used is environmentally friendly as its only consumes non toxic chemicals only. So, it is much more convenient for the large scale production in the industry.

1.3 RESEARCH OBJECTIVE

The main objective of this research is to identify the optimum condition to produce amorphous silica from sugar cane leaves by chemical extraction method.

1.4 SCOPE OF STUDY

The research is about to synthesis the amorphous silica using chemical extraction method. The scope of this research is to study the production of amorphous silica by using different extraction temperatures, different solvent of extraction, and different extraction time.

Several temperatures selected were used in order to determine the yield of the silicon dioxide contents. Other than that, this research also, is conducted to determine the amount or percentage of amorphous silica produce from varying the time taken of the extraction process. In this research, different solvents were used to study the effect of solvent towards the amount of amorphous silica produce.

Extraction time give significant effect towards the result of the experiment, so in order to achieve the higher amount of amorphous silica, this research will also carry out at different extraction time. So, this research can be simplified as three main scopes which are:

1.4.1 To study the amount of amorphous silica produce at different temperatures different solvents and different extraction time.

1.5 RATIONALE AND SIGNIFICANT OF STUDY

The significant of this study is due to the advantages that will be obtained through the production of amorphous silica. This is because the raw material used to produce the desired amorphous silica is the sugar cane leaves. Sugar cane leaves is the plant that is abundantly available in Malaysia and suitable to grow in the Asian climate. Most of the sugar producing industry only used the sugar cane as their raw material but now the sugar cane leaves can be used as the raw material to produce the amorphous silica as well maximize the use of sugar cane leaf.

Other than that, this research can be one of the alternative ways to produce amorphous silica at a very low cost but for large scale production. This is due to the inexpensive and availability of the raw material used which is the sugar cane leaves. Besides that, by producing the amorphous silica from sugar cane leaves will helps to minimize waste from sugar producing industries. This is due to the residue of the processes usually is burn in open area without consider the effect on environment.

Furthermore, this research is also applying green way approach since we can transform the industrial waste to be the raw material to produce the beneficial substance such as the amorphous silica. We can produce a product as well as protect our environment from the solid waste and open burning process that may harm the environment.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Amorphous silica was produced by several previous researches. They were using different approaches and different raw material to synthesis the amorphous silica. This is due to the high demand of this silicon dioxide and it is widely used in various industrial fields.

2.2 SUGAR CANE LEAF

Sugar cane is refer to the species of the tall perennial grasses of the genus *Saccharum* which is include family *Poachae* and family *Andropogoneae* . The sugar cane is economically important as other seed plant family such as maize, wheat and rice. According to Food and Agricultural Organization (FAO), the sugar cane is cultivated for about 20 million hectares in more than 90 countries. In India, they produce for about 320 million of agricultural residue, mainly wheat, paddy straw and cane leaf. It is estimated that for about 100 million tones of this agricultural residue were not utilized properly and were dispose by open burning (Rajeev and Rajvanshi, 1997).

The sugar cane leaf is one of the important parts of the sugar cane. The leaves can be one to two meter long. This sugar cane leaf is divided into two parts which is sheath and blade and it is separated by a blade joint. The sugar cane leaves usually attached alternately to the nodes forming two ranks on opposite sides (Combes, 2010). Normally, the mature leaves has an average total upper leaves of about 0.5 m^2 and the number of leaves in each stalk is around ten, depending on variety and growing condition.

According to Saska and Gray, (2006), the sugar cane leaf and bagasse which is the fiber of the stalk plant has been the most studied as the large biomass potential leaves. Besides that, the tops of the sugar cane plant have been recognizing to yield biomass dry solid. Based on the weight basis, it is reported by Saska and Gray, (2006) that the sugar cane leaves would be able to makes up to 25 to 40 % of biomass dry solid.

2.3 AMORPHOUS SILICA

According to Dongmin et al., (2010), the SiO_2 is the demand raw material nowadays. It is widely used in electronic, ceramic and polymer material industries. This is due to its small diameter it is use for many technological applications such as thermal insulators and composite fillers. Besides that, silica is also used as flow agent in powdered food to absorb water in hygroscopic applications. Silicon dioxide is also the primary components of the rice husk.

Thin films of silica grown on silicon wafers by the thermal oxidation methods is beneficial in microelectronics, whereby it is functioning as electric insulators with high chemical stability. In electrical applications, the silicon dioxide will protect the silicon, store charge, block current, and also act as a controlled pathway to limit the current flow based on Riordan (2007) findings.

The main characteristic of amorphous silica are mainly gives a good dimensional stability virtually no expansion or contraction. Besides that, it is also a good chemical purity and high hardness. The application of amorphous silica is mainly as abrasive materials, fillers for painting, fillers for manufacturing insert or cores for investment casting process, fillers for resin, and raw material for slip cast parts and vacuum deposition process for coating of optical lenses. Nowadays, much of the research current effort is to produce the low cost solar grade silicon by upgrading the metallurgical grade silicon or by chemical vapor phase refining. However, the essentially modifications of the classical Siemens process in making the silicon is highly and pure but prohibitively expensive.

2.4 SOURCES OF AMORPHOUS SILICA

Amorphous silica is one of the demand raw material nowadays especially by the chemical industry. Amorphous silica has wide usage in various kinds of industry. In the chemical industry, the molecular biologists employ amorphous silica in the production of resin and optical beads. While in the other industry it is used as the raw material to produce many types of products such as, glass, porcelain, chips and also used in the semiconductor circuit. This is due to its special properties of mechanical resistance and high dielectric strength.

The sources of amorphous silica usually contain in the green leaves. There are several other sources of silicon dioxide which is in the rice husk ash (RHA), potatoes, milk, drinking water and mineral water. This is due to the climate factor in Malaysia that is suitable to grow the sugarcane. Since the sugar cane leaf is abundantly available in Malaysia, the sugar cane leaves can be taken as one of the source of the amorphous silica. In order to solve problem faced by sugar producing industry this research was used the sugar cane leaf as an alternative source of amorphous silica by using chemical extraction method as reported by Farook and Anwar (2011).

Among the known polymorph of amorphous silica quartz and quartzite rocks are the most stable that can be found in most mineralogical rocks as relatively pure. Natural Dust Insecticides stated that the natural silica come from two main sources which are from heating the ordinary sand to the high temperature and diatomaceous earth that comes from skeleton of small marine organisms.

Besides that, 25.7 % of the earth crust was made from silica. The silica is the second most abundant elements in earth crust besides oxygen. Most of this silicon is not exist freely in nature, but it eventually in the form of oxides and silicates. Some of the examples of the silicon in oxides form were rock crystal, quartz, amethyst and flint. For silicates, the silica exists as granite, asbestos, clay, mica and feldspar.

2.5 PRETREATMENT AND EXTRACTION METHODS

For the pretreatment, the silica was prepared by washing in the methanol bath followed by H_2O_2. This solution was immersed for 3 days in nitric acid to removed impurities (Jonathan and Patricia, 2000). According to the result obtained by Dongmin et al., (2010) the gross weight of the silicon dioxide in the rice husk ash was 74.88 wt%. This clearly indicates that the preliminary leaching is an effective way to remove most of metallic impurities of the rice husk extracts.

According to Saska and Gray, (2006) the sugar cane leaves were separated from the sucrose containing stalk. The particle size of the loose leafy material was reduced by grinding it using shredder equipment followed by passes through the roll mill to further reduce the particle size. Based on the result obtained, the two step pretreatment combining low temperature lime impregnation at moderate pH which is 5 was found effective for pre-treatment of sugar cane biomass.

Based on Yogendra et al., (2011) findings, the pretreatment of the *Seabukthorn* leaves were made by soaking the *Seabuckthorn* leaves sample in the distilled water at room temperature before it is extracted using subcritical water extraction. Based on the result obtained, the subcritical water extraction was selected as a better approach of extraction method for *Seabuckthorn* leaves due to the imparted higher antioxidant and cytoprotective activities to the extracts compared to soxhlet and maceration technique.

2.6 THE INFLUENCE OF PARAMETERS TOWARD SILICON DIOXIDE YIELD

2.6.1 Extraction time as parameter

The extraction time gives the significant result to the yield of amorphous silica. For instance, Dongmin et al., (2010) varied the extraction time from 2 to 9 hours and the yield of silica increasing with the increasing extraction time. From the result obtained, the percentage of silica yield is gradually increasing when the concentration of Na_2CO_3 increasing. Besides that, by increasing the time for the extraction time, the result showed that, the yield of the amorphous silica is also increasing. So, this research want to upgrade and continue the research that already done by the previous researcher so that, the optimum condition for producing the amorphous silica can be determined.

2.6.2 Different types of solvent used for extraction process

Based on the findings, the methanol was chose as the best solvent for *Epidemium* leaves extraction. This is due to the high extraction yield of Epimedin C extract. The lower boiling point of methanol compare to the other solvent use might be one of the factors that lead to the higher extraction obtained. The heating effect on the extraction system may lead to the evaporation process of the methanol solvent that will leach out the Epimedin C content of the leaves (Zhang et al., 2009).

2.6.3 Extraction temperatures as parameter

The extraction process carried out by Zhang et al., (2009) reported that, the best temperature for extraction of *Epimedium* leaves is 45 °C. This is probably due to the improvement of mass transfer value resulting from the increasing of Epimedin C solubility and decrease in solvent viscosity. According to Yogendra et al., (2011), the parameter can be modulated easily by tuning the extraction temperature. This is due water as a very polar solvent. The dielectric constant of water is almost reached to 80, and this value is similar to ethanol for soluble less polar compound.

2.7 THE ANALYSIS OF AMORPHOUS SILICA COMPOSITION AND CHARACTERIZATION

According to Jonathan and Patricia (2000), the chemical composition of SiO_2 is the highest as determined from ICP-AES. Besides according to Dongmin et al., (2010), the composition of the SiO_2 is the highest compared to other substance inside the rice husk.

Table 2.1: The composition of Rice Husk Ash (RHA)

Composition	Value
K_2O	1.46 wt%
CaO	0.45 wt%
Na_2O	0.09 wt%
MgO	0.17 wt%
Al_2O_3	0.42 wt%
ZnO	0.08 wt%
Fe_2O_3	0.19 wt%
MnO_2	0.10 wt%
CuO	375 ppm
TiO_2	13 ppm
SiO_2	78.44 wt%
C	18.24 wt%
Others	0.36 wt%

Sources: Dongmin et al., (2010)

Referring to the Table 2.1, the highest content of rice husk is silicon dioxide compound which about 78.44 wt%. This shows that, the silicon dioxide is presence in the rice husk and the rice husk could be one of the sources of amorphous silica.

The broad band around 3448-3456 cm^{-1} shows the stretching vibration of Si-OH bond and the strong band at 1636-1637 shows the vibration of trapped water molecule. Strong band of 1076-1091 cm^{-1} indicate the tetrahedron Siloxane bond (Si-O-Si). The appearance of the 971-975 peaks shows the molybdenum species that prefer to be on the silica surface (Farook and Anwar, 2011).

The broad angle is due to the structural collapse due to the agglomeration of silica. At higher pH usually silica is negatively charge and will repel each other. Thus, it will avoid the agglomeration of silica particles. The colliding silica particles might be stick together to form agglomeration towards the deterioration of the pore order as stated by (Farook and Anwar, 2011).

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

In order to produce amorphous silica by using chemical extraction method, several steps must be taken into considerations. The appropriate methodology is significant for conducting experimental research so that the most accurate results can be obtained. This chapter also will describe the methodology used for the extraction process of the sugar cane leaf from the pre-treatment method until the characterization of the cane leaf.

3.2 MATERIALS AND EQUIPMENTS

3.2.1 Raw material

The sugar cane leaves were collected from Felda Lepar, in Gambang, Kuantan. The leaves were dried by sun drying for 24 hours. The dried leaves were further cut into small pieces before further dry in an oven for another 12 hours.

3.2.2 Reagents and Apparatus

Table 3.1: Reagents and Apparatus used in the experiment

3.2.2.1 Reagent	Purity	Function
1. Industrial Grade Ethanol (Fisher Chemical, USA)	95%	Used as the solvent for extraction

2. Methanol (Fisher Chemicals, USA)	99%	Used as the solvent for extraction
3. Hydrochloric Acid (Fisher Aldrich, USA)	0.3 M	Used in the pretreatment process.
3.2.2.2 Apparatus	**Brand**	**Function**
1. Soxhlet extractor unit		Used for Extraction of sugar cane leaves
2. Dessicator		To cool the dried sugar cane leaves.
3. Rotary Evaporator	Buchi Rotavapor R-200, Switzerland Rotary evaporator	To remove solvent from extracts.
4. Oven	Thermo electron corporation.	To dry the sugar cane leaves
5. Freezer	Juscool freezer 4°C, Revco Thermo Scientific -20°C Freezer	To keep the extracts obtained
6. Grinder	Retsch ZM200 Chemitel Grinder, Interscience Sdn. Bhd.	To reduce the size of sugar cane leaves in the form of ash
7. FT-IR	Nicolet Avatar 370 PTGS	To analyze the compound of sugar cane leaves extracts

3.3 MOISTURE CONTENT OF SUGAR CANE LEAVES ASH

The fresh sugar cane leaves were clean under running cool water to remove the dust and other substances deposited at the surface of the leaves. The fresh leaves were wiped dry by using a clean cloth to remove the excess water after washing the leaves. The moisture content of the sugar cane leaf ash was determined by weighing the initial mass of the fresh sugar cane leaves. The fresh sugar cane leaves was placed in the weighing boat and weighed. The mass of the fresh sugar cane leaves was recorded. The same fresh sugar cane leaves was placed in open area to let it dry for 24 hours.

After 24 hours, the dried leaves were cut into smaller pieces and further dry in an oven at 100 °C for another 12 hours in order to ensure that all of the moisture was removed from the leaves. The dried leaves were cooled in the desiccators and weighed. The final mass of the dried leaves was recorded. The percent of weight loss of the sugar cane leaves were recorded as moisture content. The process was performed in triplicate.

The moisture content of sugar cane leaves ash was determine by calculating using the formula :-

$$Percent\ of\ moisture\ content = \frac{(m_f - m_i)}{m_f} \times 100 \qquad (3.1)$$

$$m_f = final\ mass\ of\ dried\ sugar\ cane\ leaves$$
$$m_i = initial\ mass\ of\ fresh\ sugar\ cane\ leaves$$

3.4 PRETREATMENT OF SUGAR CANE LEAVES

The sugar cane leaves need to be in the form of ash before proceeding to the extraction process. First of all, 500 g of the fresh sugar cane leaves will be placed in an open space for sun drying for 24 hours. After drying, the dried sugar cane leaves were cut into smaller pieces before further dry it. After that, the sugar cane leaves will be place in an oven at temperature 100°C to let it dry and to remove the moisture content of the leaves. Then, the dried sugar cane leaves were ground by using Retsch ZM200