



## Review: Agricultural Wastes as a Source of Silica Material

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### ABSTRACT

Silica is the most abundant components in the earth's crust and is made by way of synthesis for use in the application of technology. Silica are generally found commercially as alkoxysilane compounds (i.e such as tetraethylorthosilicate (TEOS), sodium silicate, and tetramethylorthosilicat). However, these compounds can have a negative impact on health. Thus, further approaches to find the source of silica that is safer, cheaper, and more environmentally friendly is inevitable. However, not all summary journals are thoroughly discussed the silica sources. Further, method of isolation and application of the silica from agricultural waste is limited. This paper reported studied several sources of silica derived from agricultural waste, such as rice husk, rice straw, corn cobs, and bagasse. In addition, this paper discussed also about the method of isolation of silica from agricultural waste, and its application as a catalyst.

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## 1. INTRODUCTION

Silica is the most abundant in the earth's crust, but despite abundant, silica is generally made by way of synthesis for use in the application of technology and silica is one of the valuable inorganic chemical compounds that are versatile (Londeree, 2002). Silica has been widely applied in industry as fillers in composites, electronic components, catalysts, drug delivery systems, thermal insulators, rubber, chromatography, and ceramic engineering (Hao *et al.*, 2006; Gallis *et al.*, 1999).

In some publications, silica precursors generally used commercially are alkoxy silane compounds such as, tetraethylorthosilicate (TEOS), sodium silicate, and tetramethylor-thosilicat. Nakashima *et al.* reported that acute exposure can cause death TEOS. (Nakashima *et al.*, 1998) Thus, there is a need to find a silica precursor safer, cheaper, and more environmentally friendly. (Fadhulloh *et al.*, 2014). Natural silica, particularly those found in agricultural waste, can be used as an alternative source to replace the commercial silica precursors. Rice husk (Della *et al.*, 2002; Liu *et al.*, 2010; Athinarayanan *et al.*, 2014), rice straw (Zaky *et al.*, 2008; Wattanasiriwech *et al.*, 2010), corn cob (Velmurugan *et al.*, 2015; Shim *et al.*, 2015) and bagasse (Usman *et al.*, 2014; Vaibhav *et al.*, 2014) is an agricultural waste as a source of silica which has been researched and transformed into more valuable products.

In this paper, we discussed the silica source derived from agricultural waste and extraction method. This paper consisted of three parts: introduction containing information about silica and applications. In the second part, we discussed various silica sources derived from agricultural waste and the extraction method. The third part contained the result of the synthesis of silica derived from agricultural waste.

Soltani *et al.* examined only the application of rice husk, the technology used

to produce silica from rice husk, an explanation of the various furnaces to produce rice husk ash and technology to produce activated carbon from rice husk. (Soltani *et al.*, 2015) Here in this review, we discussed the potential silica source that can be obtained from agricultural waste. such as rice husks, rice straw, corn cobs, and bagasse. We also discussed extraction method.

In our previous studies, we have reviewed several methods for extracting several materials, such as silica (Fadhulloh *et al.*, 2014), titania (Rahman *et al.*, 2014), carbon (Rahman *et al.*, 2015), nanoselulosa (Effendi *et al.*, 2015), and fotokatalis material (Sucahya *et al.*, 2016). Here, the purpose of this paper was to provide a discussion of the silica source derived from agricultural waste and its application more thoroughly. With the information through this paper, we expected that related industries can use agricultural waste as a source of silica in order to reduce the production costs as well as gain a positive impact for the environment (due the reduction of waste).

## 2. CURRENT STUDIES ON THE USE OF SILICA SOURCE AND METHOD FOR EXPLOIT SILICA COMPONENT

Several agricultural wastes that can be used as a source of silica can be seen in **Table 1**. **Table 1** shows that rice husk, rice straw, corn cobs, and bagasse can be used as a source of silica. Whilst, the methods used are chemical treatment, thermal treatment, and microbial treatment.

## 3. METHOD FOR EXTRACTING SILICA FROM AGRICULTURAL WASTE

There are three main methods for producing silica from agricultural waste, i.e. chemical treatment, thermal treatment, and microbial treatment. (Fadhulloh *et al.*, 2014) The first stage is done in the

extraction of silica in agricultural waste by acid leaching (Adam *et al.*, 2008; Adam *et al.*, 2011; Ding & Su, 2012; Li *et al.*, 2011; Ang *et al.*, 2012; Zulkifli *et al.*, 2012; Gu *et al.*, 2013; Noushad *et al.*, 2014; Kongmanklang & Rangriwatananon, 2015, Kumar *et al.*, 2015). Acid leaching of agricultural waste is used to eliminate impurities and improve the purity of the silica contained therein. Organic compounds in agricultural waste and other impurities material can be converted into ions dissolved by a simple acid treatment (Vaibhav *et al.*, 2014).

Chakraverty *et al.* reported their researches on the effects of acids in removing metal impurities from rice husk. (Chakraverty *et al.*, 1988) Research conducted by comparing the levels of metal impurities from rice husks that are not treated with acid and rice husks were treated with HCl, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub>. The rice husks which are not treated metal levels have very high of sodium, potassium and calcium compared to ferrous metals, magnesium, manganese, zinc, and copper. In contrast, the rice husks which are treated with acid, metal levels decrease. From the three acid used (HCl, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub>) showed HCl is the most effective chemical for removing metal impurities from rice husks. The studies showed that rice husk dissolved in HCl (1N) produce a white colored ash. The effect of the reduction of acid and metal impurity concentration is shown in **Table 2**.

Rafiee *et al.* reported the HCl in the stages of acid leaching can effectively done at concentration of 1 M for removal of metal with a surface area and the pore volume generated is also good. (Rafiee *et al.*, 2012) Other researchers have reported the used of alkali-acid treatment to purify silica in agricultural waste. Ding and Su reported the production of mastoid SiO<sub>2</sub> with different crystal structures with other SiO<sub>2</sub> crystal. (Ding & Su, 2012) The first stage of their

research is purification with acid and alkaline pre-treatment. The first objective of refining is to remove the metals Na, Mg, Ca, Mn, Al, Fe, Zn, and other elements with acidic water (consisting of 30 % H<sub>2</sub>O<sub>2</sub> and 10 % HCl). The second objective is to remove the metals Na, Cl, P, S, and other elements with alkaline water (consisting of 30 % NH<sub>3</sub>.H<sub>2</sub>O). The purified rice husks are washed and heated at a temperature of 600<sup>0</sup>C for 10 hours to obtain a white silica product. Finally, a white powder SiO<sub>2</sub> can be obtained by ultrasonic fragmentation method. However, the use of strong acid in acid leaching causes negative impacts to the environment. In addition, the use of strong acid also becomes economical problems because the price of acid is expensive. Therefore, other experiments using acids that give more benefits, i.e. environmentally friendly, harmless, and more economical (Umeda & Kondoh, 2008; Umeda & Kondoh, 2010).

Umeda and Kondoh using a carboxylic acid (citric acid) and hydrolysis process at temperatures above 200<sup>0</sup>C to produce high-purity silica. (Umeda & Kondoh, 2008) Metal impurities such as Na, K, Ca, Mg, Fe, and Cu can be removed from rice husk through a chelate reaction between the carboxyl group (-COOH) to metal. After the acid leaching process, providing a number of air for complete combustion of the organic process is essential. From the experimental results using citric acid, amorphous silica can be obtained with a purity of 99%.

Real *et al.* stated that the process of acid leaching in rice husks before burning produce silica powder with a large surface area. (Real *et al.*, 1996) However, if the acid leaching stage is carried out after the combustion process, the surface area of the silica is not so high.

**Tabel 1.** Materials, researcher, methods, and results of isolation silica.

Materials	Research Group	Methods	Result	Reference
Rice Husk	Kamath and Proctor	Chemical treatment	Rice hull silica gel with a surface area of 258 m <sup>2</sup> /g and a particle size of < 5 to > 40 μm	Kamath and Proctor, 1998
	Kalapathy <i>et al.</i>	Chemical treatment	Silica with a purity of 91%	Kalapathy <i>et al.</i> , 2000
	Liou <i>et al.</i>	Chemical treatment	Silica with a surface area of 634 m <sup>2</sup> /g, pore diameter of 3 to 9 nm, the particle size of 5-30 nm	Liou, 2011
	Yuvakkumar <i>et al.</i>	Chemical treatment	Nanosilica powder with a purity of 99%, a particle size of 25 nm, a surface area of 274 m <sup>2</sup> g <sup>-1</sup>	Yuvakkumar <i>et al.</i> , 2012
	Della <i>et al.</i>	Thermal treatment	Silica with a surface area of 81 m <sup>2</sup> /g	Della <i>et al.</i> , 2002
	Witoon <i>et al.</i>	Thermal treatment	Porous silica with a pore diameter of 4.30 nm and 10 nm at pH 3 and 7.70 nm and > 30 nm at pH 5	Witoon <i>et al.</i> , 2008
	Li <i>et al.</i>	Thermal treatment	Porous silica with a surface area of 1018 m <sup>2</sup> /g, pore diameter of 2.30 nm	Li <i>et al.</i> , 2011

**Tabel 1.** (continued) Materials, researcher, methods, and results of isolation silica.

Materials	Research Group	Methods	Result	Reference
Rice Husk	Adam <i>et al.</i>	Thermal treatment	Porous silica with a surface area of 245 m <sup>2</sup> /g, pore size of 5.60 to 9.60 nm	Adam <i>et al.</i> , 2011
	Zulkifli <i>et al.</i>	Thermal treatment	Mesoporous silica with a surface area of 364, 35 m <sup>2</sup> /g, particle size of 72 to 252 nm	Zulkifli <i>et al.</i> , 2013
	Umeda and Kondoh	Thermal treatment	silica obtained as much as 99.50 to 99.77%	Umeda & Kondoh, 2010
	Gu <i>et al.</i>	Thermal treatment	silica obtained as much as 99.92%	Gu <i>et al.</i> , 2013
	Rohatgi <i>et al.</i>	Microbial treatment	silica obtained as much as 49.00%	Rohatgi <i>et al.</i> , 1987
	Esteves <i>et al.</i>	Microbial treatment	Silica with a particle size of 55 to 250 nm	Esteves <i>et al.</i> , 2009
Rice Straw	Zaky <i>et al.</i>	Chemical treatment	Silica with a particle size between 50 and 70 nm	Zaky <i>et al.</i> , 2008
	Hessien <i>et al.</i>	Chemical treatment	Silica with a particle size between 16 and 18 nm	Hessien <i>et al.</i> , 2009
	Khorsand <i>et al.</i>	Chemical treatment	Silica nanoparticle with a diameter of 10-15 nm and a surface area of 327 m <sup>2</sup> /g	Khorsand <i>et al.</i> , 2012

**Tabel 1.** (continued) Materials, researcher, methods, and results of isolation silica.

Materials	Research Group	Methods	Result	Reference
Rice Straw	Lu and Hsieh	Thermal treatment	Silica nanodisk with a surface area of 509, 50 m <sup>2</sup> /g and a pori size of 5,80 nm	Lu & Hsieh, 2012
	Wattanasiriwech <i>et al.</i>	Microbial treatment	Silica with a particle size between 50 and 80 nm	Wattanasiriwech <i>et al.</i> , 2010
Corn Cobs	Velmurugan <i>et al.</i>	Chemical treatment	Silica amorf with a particle size of 50 nm	Velmurugan <i>et al.</i> , 2015
	Shim <i>et al.</i>	Chemical treatment	silica obtained as much as 99,50%	Shim <i>et al.</i> , 2015
Bagasse	Vaibhav <i>et al.</i>	Chemical treatment	silica obtained as much as 71%	Vaibhav <i>et al.</i> , 2014
	Usman <i>et al.</i>	Thermal treatment	silica obtained as much as 77,286%	Usman <i>et al.</i> , 2014

Silica can be extracted from rice husk using the chemical treatment methods; solubility of amorphous silica is very low at pH < 10 and increases sharply at pH > 10. This causes the silica may be extracted in pure form by dissolving it in the base state and then deposited in acidic conditions (low pH) (Kamath & Proctor, 1998).

Silica obtained by chemical treatment method has a high purity, but the process is complex and uses many reagents. Instead of these methods, pyrolysis method is more attractive because preparation process is simple and using lower cost (Gu *et al.*, 2013). Researchers use a method of thermal treatment in the

extract silica in rice husk (Chakraverty *et al.*, 1988; Della *et al.*, 2002; Zulkifli *et al.*, 2013; Gu *et al.*, 2013; Kongmanklang & Rangriwatananon *et al.*, 2015). Other researchers suggested a method to remove silica particles in the rice husk through microbial fermentation using fungi and worms (Rohatgi *et al.*, 1987; Esteves *et al.*, 2009).

Overall, the structure and properties of silica derived from agricultural waste is strongly influenced by the extraction method used. Morphology obtained either amorphous silica or crystals depend on the temperature or chemical treatment (Soltani *et al.*, 2015).

**Table 2.** Acid leaching effect of the removal of metals from rice husk. Adopted from reference (Chakraverty *et al.*, 1988)

Treatment	Metallic ingredients as oxides (p.p.m.)								
	Na	K	Ca	Fe	Mg	Mn	Zn	Cu	Total
Untreated	5125	11 750	7042	946	2562	1192	179	31	28 827
1 N HCl treated	46	50	58	362	187	19	19	6	747
3 N HCl treated	33	33	46	262	146	7	19	6	552
5 N HCl treated	25	HD	25	146	125	3	19	6	349
11.3 N HCl treated	12	HD	8	129	125	3	17	6	300
1 N H <sub>2</sub> SO <sub>4</sub> treated	87	25	2500	233	729	25	102	12	3 713
4.5 N H <sub>2</sub> SO <sub>4</sub> treated	92	25	2417	225	646	25	98	6	3 534
9 N H <sub>2</sub> SO <sub>4</sub> treated	75	25	2500	229	625	19	85	6	3 564
18 N H <sub>2</sub> SO <sub>4</sub> treated	75	50	2667	217	625	24	83	6	3 747
36 N H <sub>2</sub> SO <sub>4</sub> treated	117	100	3333	221	437	171	98	6	4 483
4.5 N HNO <sub>3</sub> treated	17	25	19	500	83	19	17	8	688
9 N HNO <sub>3</sub> treated	8	25	11	442	83	12	12	6	599
18 N HNO <sub>3</sub> treated	4	25	7	392	62	6	12	HD	508
1 N HCl + 4.5N HNO <sub>3</sub> (1:3)	4	25	3	375	52	12	19	6	496

### 3.1. Rice husk as a source of silica

Rice husk is a by-product of rice milling industry and represented 20% of the weight of the rice (Ang *et al.*, 2012). The main inorganic component in rice husk is silica (~20%) (Rohatgi *et al.*, 1987). Extraction of silica from rice husk is a growing trend in the respiratory diseases if inhaled by human (Vaibhav *et al.*, 2014). Therefore, recycling waste and recreating it into a high-value material are important because we can gain not only beneficial for the environment but also as a promising resource. Due to the high silica content in the rice husk, rice husk utilization as a raw material for the production of products using silica is an interesting issue this time (Gu *et al.*, 2013).

### 3.2. Rice straw as a source of silica

Rice straw is the stem of rice plants that are separated during the rice harvest and considered as agricultural waste. Rice straw available in large quantities and does not have a commercial interest (Zaky *et al.*, 2008). Rice straw is one of the agricultural waste that is rich in silica (Agbagla-Dohnani *et al.*, 2001; Hessien *et al.*, 2009). The content of silica in the rice straw is larger than other plants. Organic components in rice straw is cellulose (32-47%), hemicellulose (19-27 %), lignin (5-24 %), and ash (13-20 %) (Santos *et al.*, 2010). Ash constituents depend on the type of rice, climatic, and geographical conditions where rice is grown (Zaky *et al.*, 2008).

### 3.3. Corn cobs as a source of silica

Corn cobs is an agricultural waste obtained from corn. Corn cobs contain more than 60 % silica with small amounts of metal (Adesanya & Raheem, 2009). Corn cobs can be used as an economical raw material in the production of silica. Ash corn cob obtained in the form of a fine powder after combustion so that it does not require further grinding, and corn cob ash is the most economical source of silica (Velmurugan *et al.*, 2015).

field of current research. Most of the rice husk is treated only as waste and disposed to landfill, while this waste can create a fire and environmental pollution. Further, particles originating from the dust produced from burning rice husks can cause

### 3.4. Bagasse as a source of silica

Bagasse is one agricultural wastes containing silica. Vaibhav *et al.* produced silica nanoparticles originating from agricultural waste, one of which is bagasse. (Vaibhav *et al.*, 2014) The method used is dissolution by alkaline NaOH and precipitation by sulfuric acid. EDAX analysis results indicate that the silica with levels high enough and a little impurities such as potassium and calcium magnesium. From the research, the silica obtained from bagasse by 71.

## 4. EXPERIMENTAL RESULT FROM THE USE OF VARIOUS SILICA SOURCES

### 4.1. Rice husk

Kalapathy *et al.* extracted silica from rice husks which is preceded by leaching stage to remove impurities, followed by dissolution of the silica with the addition of NaOH solution to form a solution of sodium silicate. (Kalapathy *et al.*, 2000) The next stage is the deposition of silica in sodium silicate solution through acid treatment using hydrochloric acid (HCl). The results obtained are dried at a temperature of 80°C for 12 hours. From the results of these experiments are successfully extracted silica of about 91%. However, the resulting silica still contains 4% sodium as impurities and requires a washing step back to reduce the concentration of sodium to below 0.10%. This causes the process is long and not effective. To overcome this, Kalapathy *et al.* developed a method for reducing the sodium in the silica impurities. (Kalapathy *et al.*, 2002) In the previous study, silica produced at alkaline pH needed a washing stage after drying aquagel (Kalapathy *et al.*,



2000). Development of the method in this study does not require washing steps back to produce silica. The research is to produce silica as sodium silicate at pH 4 by adding sodium silicate into a solution of citric acid, oxalic acid, or hydrochloric acid and comparing purity silica produced at pH 4 and pH 7 (obtained by adding an acid solution into a solution of sodium silicate). The results showed that at pH 4, gelation occurs more slowly. So that sodium ions can diffuse rapidly out of the gel matrix therefore lower sodium content than the silica extracted at pH 7. Due to pH 7, gelation occurs rapidly to make sodium ions trapped in a gel matrix. Silica deposition using citric acid and oxalic acid to produce sodium silicate levels were lower compared with silica precipitated by hydrochloric acid. This is due to differences in the size of the sodium salt. Because of the small size of the sodium chloride salt, sodium chloride can be absorbed on the surface of microporous silica and can not be removed by washing. Therefore, the sodium levels increase. Silica obtained from pH 4 to 7 are in the range 89-91% with an average water content of 2.30%.

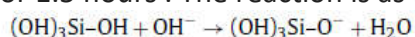
Liou *et al.* reported that the acid treatment affects on the surface area of the silica obtained. (Liou *et al.*, 2011) Research carried out by using hydrochloric acid (HCl), sulfuric ( $H_2SO_4$ ), oxalate ( $C_2H_2O_4$ ), and citric acid ( $C_6H_8O_7$ ) to precipitate silica in sodium silicate solution. The results showed that the minimum surface area occurs in silica extracted using citric acid. The surface area increases as the silica precipitated by sulfuric acid or oxalic acid. Furthermore, the surface area reaches a maximum condition when the silica precipitated by hydrochloric acid. Acid sequence with a surface area of the largest to the smallest was HCl,  $H_2SO_4$ ,  $C_2H_2O_4$ , and  $C_6H_8O_7$ . The salt with larger size can be trapped in a gel matrix that can not be washed out when it causes pores and reduces the surface area covered (Yun *et al.*, 2003). The results showed that the optimum candidate acid is hydrochloric acid to

precipitate silica. In addition, this research also studied the effect of variations in gelation pH of 1 to 11 on the surface area of the silica. The surface area of the silica is strongly influenced by the pH value. With decreasing pH, the surface area silica increase. They reported that gelation does not occur at a pH of less than 3. At pH = 3, solids begin to settle, while the gel formation is slow. Silica obtained increases with increasing pH, the maximum yield is obtained at a pH of about 7. When the pH is greater than 8, gel formation was unstable and partially dissolved back. At pH 11, the gel is almost completely dissolved. On the other hand, gelation pH has a great influence on the porosity and size of the particles of silica produced. When the pH is increased from 3 to 7, the particle size and porosity increase because during the formation of a gel, a polycondensation reaction can occur in two consecutive lines (Munoz-Aguado & Gregorkiewitz, 1997).

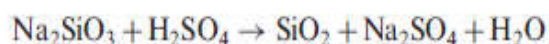
OH<sup>-</sup> has an important role. In the regime of acid, reducing the pH gelation leads to the conversion of a siloxane bond (Si-O-Si) into bonding silanol (Si-OH) and slow gel formation. In such situations, the silica consisting of primary particles is small and therefore, has a large surface area. In a basic understanding, formation of surface silanol siloxanes to form a negative charge between the particles of silica and lead to increased electrostatic repulsion (Schlomach & Kind, 2004). Catalyzes the charge particles to grow further, resulting in an increase in particle size with increasing pH. These results lead to an increase in porosity and decrease the surface area of the sample.

Yuvakkumar *et al.* reported the results of their research in producing high-purity powder nanosilica from rice husk using a chemical treatment is extraction with alkaline and acid precipitation. (Yuvakkumar *et al.*, 2012) In their research, they studied the initial treatment and the effect of the concentration of sodium hydroxide (NaOH) to the powder purity nanosilica. Rice husk

through several stages to remove impurities that rice husk obtained were washed with water to remove impurities, then dried at room temperature and then burned at a temperature of 973K for 3 hours. Rice husk ash obtained is then washed with water and then refluxed with hydrochloric acid. The result is then filtered to remove metal impurities, the filtrate obtained is then boiled together with various concentrations of NaOH solution at a temperature of 353K for 1.5 hours. The reaction is as follows :



Sodium silicate solution ( $\text{Na}_2\text{SiO}_3$ ) obtained are then precipitated with sulfuric acid. The reaction can be written as



Precipitated silica which is obtained is then washed in warm distilled water and filtered. The residue obtained is heated at a temperature of 973K and 1373K for 3 hours in a furnace. From the experimental results obtained optimum concentration of 2.5 N NaOH with nanosilica resulting powder having a purity of 99.90%, an average particle size of 25 nm, and a surface area of  $274 \text{ m}^2 \text{ g}^{-1}$ . From this study, the factors affecting the purity silica is the optimum time, the number of wash cycles, the temperature, and the concentration of NaOH solution. Purity of silica increases when the wash cycle increases, compared the results of this research with the research conducted by Liou *et al.* and Conradt *et al.* that only one washing cycle in which the purity silica obtained only 95%. (Liou *et al.*, 2004; Conradt *et al.*, 1992)

Della *et al.* reported the results of their research on the characterization of silica derived from rice husk through thermal treatment at various temperatures (400 -  $700^\circ\text{C}$ ). (Della *et al.*, 2002) Rice husk burns at a temperature of  $700^\circ\text{C}$  to produce silica

of about 95 %. Silica obtained at a temperature of  $700^\circ\text{C}$  is then milled to reduce particle size. The results showed that the grinding process after the burning process can increase the silica surface area of  $54 \text{ m}^2/\text{g}$  to  $81 \text{ m}^2/\text{g}$ .

Witton *et al.* synthesized bimodal porous (mesoporous and microporous) silica from rice husk through sol - gel method using chitosan as a template with a variation of pH 2-6. (Witton *et al.*, 2008) Witton *et al.* reported that the porous silica synthesized by the template chitosan generate pores with a diameter of 4.30 nm and  $> 10\text{nm}$  at pH 3 and 7.70 nm and  $> 30 \text{ nm}$  at pH 5. Silica porous template chitosan has a pore size distribution wider than the silica synthesized without template chitosan. The surface area, pore diameter, and pore volume of the silica products synthesized with no template chitosan and chitosan are shown in **Table 3**.

The results showed that the presence of chitosan can increase not only surface area but also pore volume compared to products without chitosan. Additionally, the chitosan increases the thermal stability of porous silica produced. Mesoporous diameter can be modified by adjusting the pH.

Li *et al.* synthesize silica from rice husk with pyrolysis method in less than 10 hours. (Li *et al.*, 2011) Silica is produced from pyrolysis of rice husk with the addition of phosphoric acid into a solution of sodium silicate. pH is varied from 3.20 to 5.70. The process involves the addition of PEG (polyethylene glycol) to form a composite silica - PEG. The reduced pH increases the amount of PEG attached to the composite silica - PEG, and therefore more pores are formed at low pH when PEG destroyed on calcination step at a temperature of  $500^\circ\text{C}$ . Silica obtained at pH 3.20 has the greatest surface area of about  $1018 \text{ m}^2/\text{g}$  with a pore diameter of 2.30 nm.

**Table 3.** Physical properties of porous silica prepared with and without a template chitosan at various pH. Adopted from reference (Witoon *et al.*, 2008).

Product <sup>a</sup>	Physical properties		
	$S_{BET}$ (m <sup>2</sup> /g)	$D$ (nm)	$V_t$ (cm <sup>3</sup> /g)
P-2*	783	3.4	0.51
P-2	43	3.4	0.05
P-3	467	4.3	0.54
P-4	433	3.8	0.44
P-5	345	7.8	0.78
P-6	235	12.4	0.95
C-2	588	3.8	0.65
C-3	489	4.3	1.08
C-4	627	3.4	0.95
C-5	380	7.7	1.36
C-6	366	14.1	1.70

<sup>a</sup>Porous silica products were prepared with (C) and without (P) chitosan template at the calcination temperature of 800 °C, designated as C-x and P-x where x is the pH of mixture.

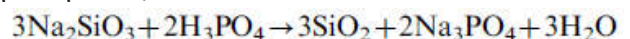
\*The sample was calcined at 450 °C.

Adam *et al.* reported the results of their research on the synthesis of spherical nanosilica from rice husks by the sol-gel method without the use of templates and calcination process. (Adam *et al.*, 2011) Their researches aim to create an inexpensive method without the use of templates that are relatively high and without using the calcination stage thus avoiding the use of high temperatures. This research does not require high temperatures because the method can be at a room temperature (~ 30°C). The chronology of the procedure in this study is shown in **Figure 1**.

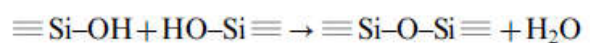
The results were obtained porous silica with a surface area of 245m<sup>2</sup>/ g and the pore volume was 0.78 cc/g. The resulting silica nanoparticles have a pore size distribution from 5.60 to 9.60 nm. From the results, TEM shows that the silica produced in the form of aggregated spherical particles with a diameter of between 15 and 91 nm.

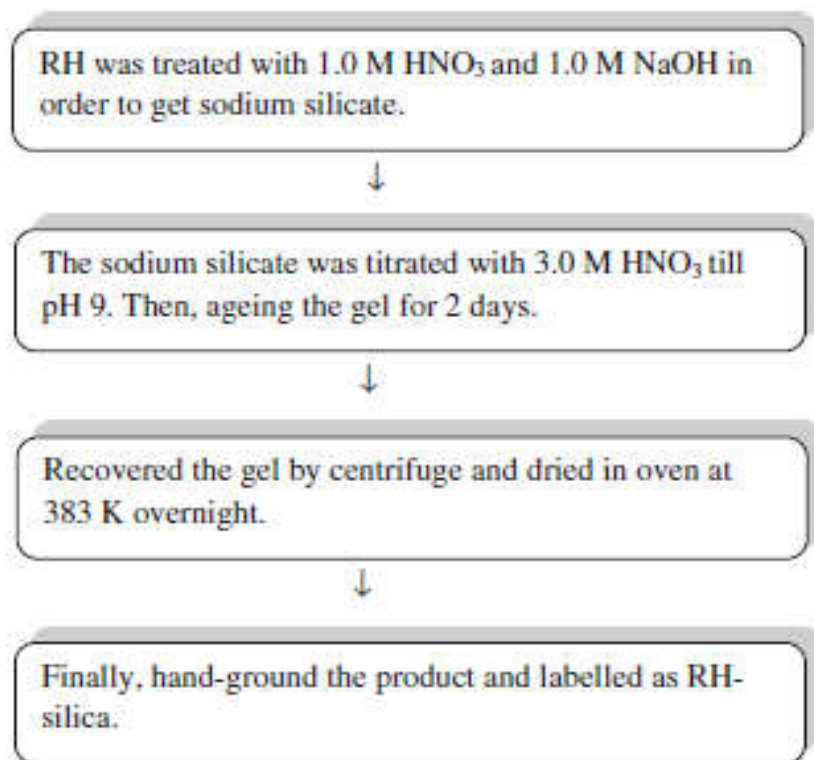
Zulkifli *et al.* in 2013 reported the results of their research in synthesizing silica nanoparticles with a spherical structure of rice husk without using a template. The surface area is greater than Adam *et al.* (Adam *et al.*, 2011). Research conducted using the sol - gel method with sodium silicate derived of rice husk as a precursor. Phosphoric acid is used as a precipitant for polyprotic properties that can control hydrolysis reaction and particle formation. Research procedure is shown in **Figure 2**.

By using phosphoric acid as a precipitant, the reaction occurs as follows :



During the addition of phosphoric acid, Si - OH formed and condensed to form siloxane bonds [ Si - O - Si ] as shown below :



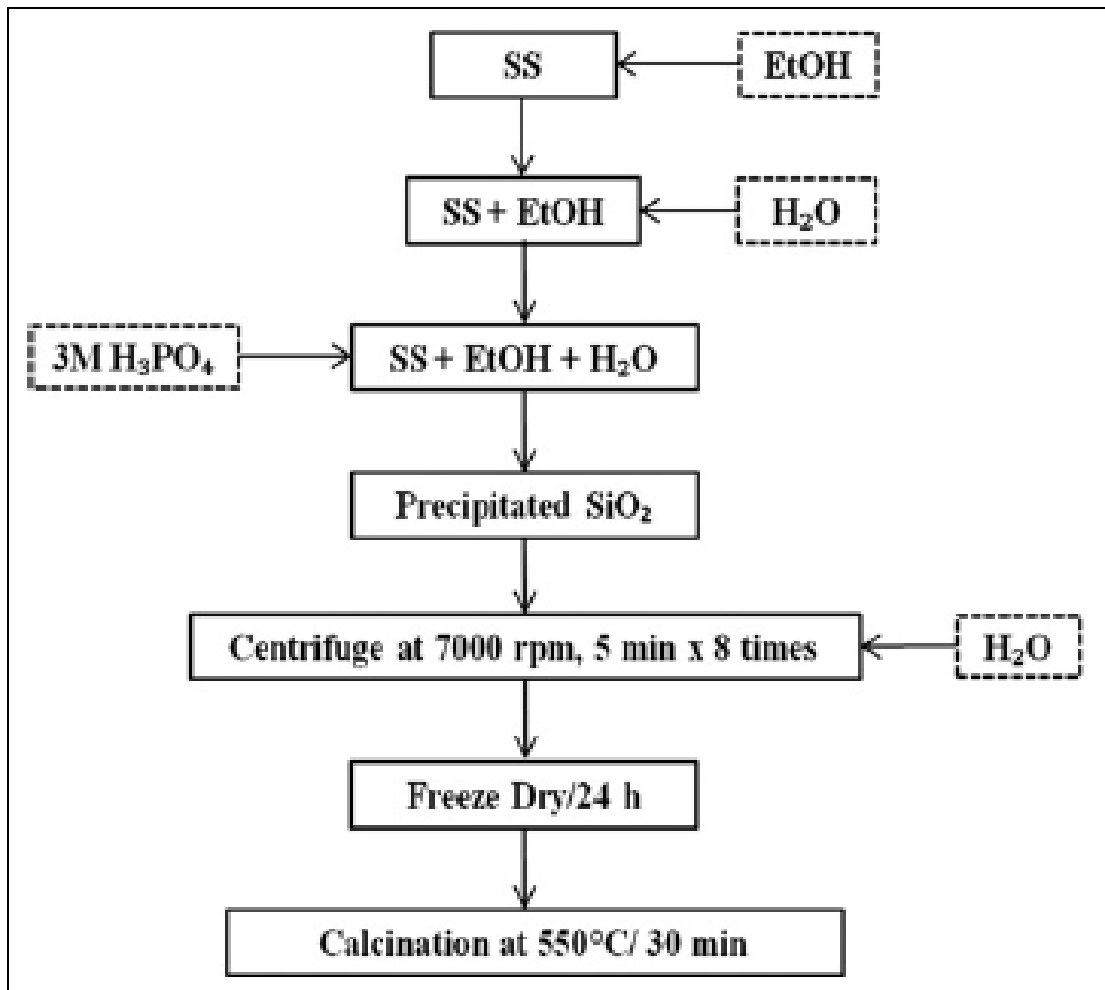


**Figure 1.** Flowchart synthesis of mesoporous nanosilica of rice husk. Adopted from reference (Adam *et al.*, 2011).

At the initial stage, Si - OH species can form dimers, trimers, or grows into primary particles. The formation of particles with different morphologies depends on the reaction conditions such as the addition of ethanol, pH variation, and addition of water. The addition of ethanol in this study show that the presence of ethanol particles leads to the form atom of particles to be more dispersed and round shape, while the particles produced without the addition of ethanol results particles agglomerated and irregular shape, but the addition of ethanol leads to a decrease in surface area from ~301 to ~72 m<sup>2</sup>/g. TEM image of silica results generated by different amounts of ethanol is shown in **Figure 3**.

Variations of pH from 7 to 9 show that the particle size increases with increasing

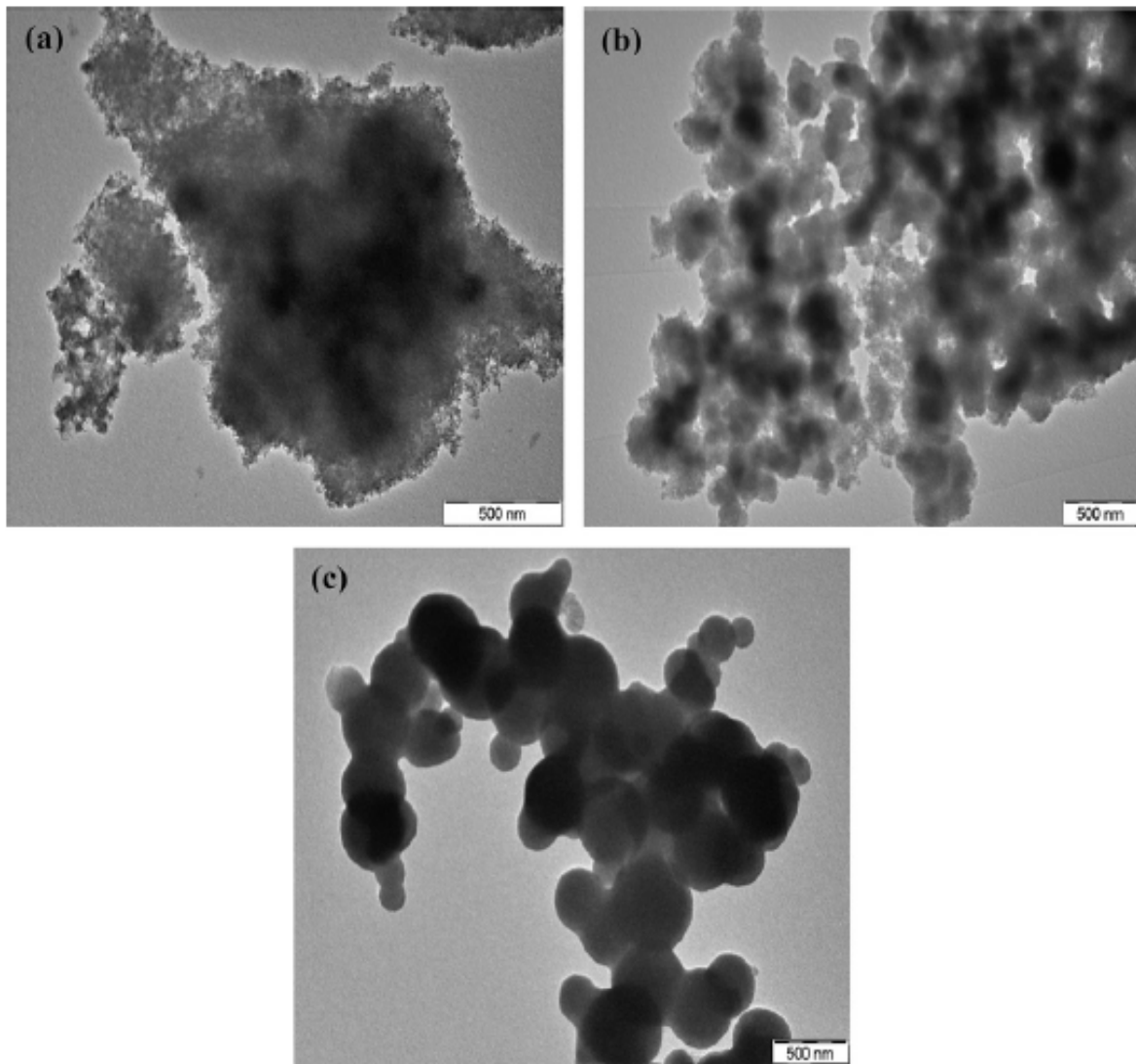
pH. TEM results indicate that the morphology of silica particles to be more sphere and particle size to be larger with increasing pH. From the analysis of the N<sub>2</sub> adsorption isotherm/desorption, silica surface area of about 197, 198, and 73 m<sup>2</sup>/g with a pore diameter of 4.89, 6.50, and 7.64 nm are obtained at pH 7, 8, and 9. The addition of water lowers the level of aggregation of particles and creates a more dispersed particle. The results also reveal that the optimal conditions for the synthesis of silica is at a ratio of 1:1:0.25 sodium silicate : water : ethanol at pH 7 with a surface area of 364.35 m<sup>2</sup>/g, a particle size of 72 to 252 nm, and particles produced in the form of mesoporous with a pore size of 7.92 nm. The overall study results are shown in **Table 4**.



**Figure 2.** Flowchart synthesis of silica using sodium silicate precursors derived from rice husk (SS = Sodium Silicate ; EtOH = Ethanol). Adopted from reference (Zulkifli *et al.*, 2013).

Umeda and Kondoh managed to extract an amorphous silica from rice husks as much as 99.50 to 99.77% through a combination of polysaccharide hydrolysis and combustion at temperatures of 1073-1273K. (Umeda & Kondoh, 2010) However, this study has shortcomings because it takes energy for combustion process. To overcome these shortcomings, Gu *et al.* to conduct research on the synthesis nanosilica of rice husk using the pyrolysis method. (Gu *et al.*, 2013) The study used a variation in temperature of 500-650°C. The survey results revealed that the pyrolysis

temperature affects on the quality nanosilica. Pyrolysis of rice husk at high temperatures reduces the carbon content and enhances whiteness of nanosilica. Level of whiteness of nanosilica increases with increasing temperature of from 500 to 610°C. However, the use of temperatures that are too high can cause damage to the Si-C bond causes increased levels of carbon and silica levels in nanosilica decline. Pyrolysis temperature optimum in this study was 610°C with a silica content of 99.92%.



**Figure 3.** TEM image of silica produced from the amount of ethanol that is different from the ratio SS : H<sub>2</sub>O : EtOH at pH 9 : (a) 1:0:0; (b) 1:0:0:15; and (c) 1:0:0:25. Adopted from reference (Zulkifli *et al.*, 2013) .

Rohatgi *et al.* suggested a method to remove silica particles in the rice husk through microbial fermentation. (Rohatgi *et al.*, 1987) Rice husk undergo microbial fermentation using white rot fungi species (*Cyathus*). Fermented rice husk was conducted for 60 days under standard conditions the availability of substrate and temperature growth. They reported that after harvesting process, husk that has been

fermented and dried at a temperature of 80<sup>0</sup>C was filtered through a sieve with a different size to separate the small particles. The filtrate is then burned at a temperature of 450<sup>0</sup>C. The results showed that fermentation resulted in a decrease in organic matter and an increase in inorganic materials (SiO<sub>2</sub>). SiO<sub>2</sub> content also increases with the small size of the filter. Results of the study are presented in **Table 5**.

**Table 4.** BET surface wide, total pore volume, pore diameter, and the particle size of the silica produced on various parameters. Adopted from reference (Zulkifli *et al.*, 2013 )

Samples	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Single point total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Average pore diameter (nm)	Average particle size (nm)	Particle size range (nm)
Effect of Ethanol					
1:0:0 <sup>a</sup>	300.82	1.17	15.56	NA	NA
1:0:0.15 <sup>a</sup>	197.66	0.48	9.72	180.67	98–272
1:0:0.25 <sup>a</sup>	73.26	0.14	7.64	288.49	94–631
Effect of pH					
pH 7 <sup>b</sup>	196.66	0.24	4.89	226.37	78–435
pH 8 <sup>b</sup>	198.49	0.32	6.50	294.79	51–607
Effect of addition of water					
1:1:0.25 <sup>c</sup>	364.35	0.72	7.92	147.49	75–252
1:1:0.25 <sup>d</sup>	357.86	0.67	7.68	164.49	37–267
1:1:0.25 <sup>e</sup>	212.45	1.21	7.7	192.00	28–317

<sup>a</sup>Samples were prepared using 3 M H<sub>3</sub>PO<sub>4</sub> at pH 9 based on ratio of SS:H<sub>2</sub>O:EtOH.

<sup>b</sup>Samples were prepared using 3 M H<sub>3</sub>PO<sub>4</sub> based on ratio of SS:H<sub>2</sub>O:EtOH=1:0:0.25.

<sup>c</sup>Samples were prepared using 3 M H<sub>3</sub>PO<sub>4</sub> at pH 7 based on ratio of SS:H<sub>2</sub>O:EtOH.

<sup>d</sup>Samples were prepared using 3 M H<sub>3</sub>PO<sub>4</sub> at pH 8 based on ratio of SS:H<sub>2</sub>O:EtOH.

<sup>e</sup>Samples were prepared using 3 M H<sub>3</sub>PO<sub>4</sub> at pH 9 based on ratio of SS:H<sub>2</sub>O:EtOH.

Esteves *et al.* produced nanosilica particles from waste rice husk through microbial treatment method using Californian red worms. (Esteves *et al.*, 2009) In their research, the worms are fed rice husks for five months. Humus which excreted neutralized with  $\text{CaCO}_3$  and calcined at various temperatures (500, 600, 700 $^\circ\text{C}$ ) and then digested with a mixture of HCl and  $\text{HNO}_3$  (1:3). Silica particles obtained by measuring 55 to 250 nm dependent on calcination temperature. From these studies it is known that to obtain a single nanoparticle, calcination temperature must be lower than 600 $^\circ\text{C}$ .

#### 4.2. Rice straw

Zaky *et al.* synthesized silica nanoparticles of semi-burned ash rice straw using dissolution method with NaOH and precipitation with sulfuric acid to form a silica xerogel which then grinded to obtain silica nanoparticles. (Zaky *et al.*, 2008) This research studied the influence of reaction time, temperature, and composition of the dissolution of NaOH:SiO<sub>2</sub> on the efficiency of dissolution. The results revealed that the dissolution efficiency increases with increasing temperature and reaction time

under different ratios of NaOH : SiO<sub>2</sub>. Zaky *et al.* reported that the solubility of silica efficiency can reach 99 % with the reaction temperature of 100 $^\circ\text{C}$ , reaction time of 4 hours, and stoichiometry of 3. TEM images indicate nanosilica particles obtained spherical with average size of 50-70 nm.

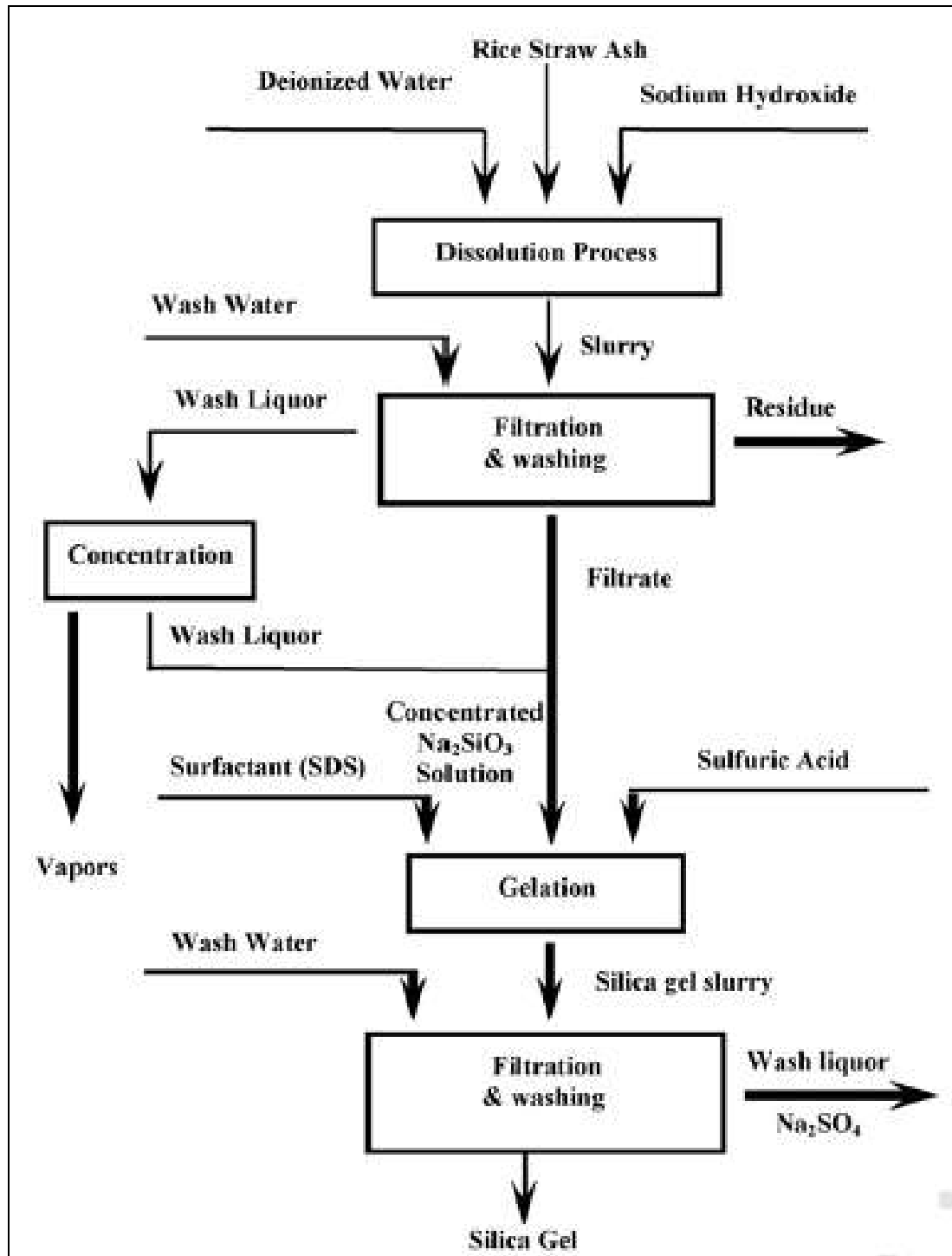
Hessien *et al.* conducted a synthesis of silica nanosphere of semi-burned rice straw using dissolution method by NaOH and precipitation by sulfuric acid. Chronology of the procedure in this study is shown in **Figure 4.** (Hessien *et al.*, 2009)

This research studied the effect of the concentration of sodium silicate, the amount of sulfuric acid, and the addition of the surfactant (sodium dodecyl sulfate (SDS)) to the particle size. The results showed a decrease in the size of the silica particles, followed by increasing concentrations of sodium silicate and SDS, while an increase in the concentration of sulfuric acid is not a big influence on changes in particle size. Optimum conditions to produce silica (30% of sodium silicate) are SDS concentration of 200 ppm and a sulfuric acid concentration of 4%. The size of silica particles produced is in the range between 16 and 18 nm.

**Table 5.** Chemical analysis of fermented rice husk and without fermented. Adopted from Rohatgi *et al.* (1987)

Sample	Sieve size	% loss on ignition at 450 $^\circ\text{C}$	% SiO <sub>2</sub> of dried material
Unfermented husk	As-received condition	74.1	23.7
Fermented husk	~ 2 mm	64.7	31.3
	- 2 mm + 85 $\mu\text{m}$	59.4	36.1
	- 850 + 60 $\mu\text{m}$	55.8	40.1
	- 600 $\mu\text{m}$	45.0	49.0





**Figure 4.** Flow diagram of the production process silica. Adopted from reference (Hessien *et al.*, 2009).

Khorsand *et al.* reported the use of rice straw ash as a source of silica. (Khorsand *et al.*, 2012) Their research is developed from Zaky *et al.*, 2008 that is dissolving with NaOH and precipitation with sulfuric acid. The obtained silica nanoparticles have diameters of 10-15 nm and a surface area of 327 m<sup>2</sup>/g.

Lu and Hsieh synthesized nanosilica disk from rice straw. (Lu & Hsieh, 2012) In this study, rice straw ash obtained by burning three stages: at a temperature of 250°C for 1 hour, then 325°C for 1 hour, and finally at a temperature of 575°C for 10 hours to remove the impurity components. Silica is extracted from the white ash with the dissolution method by NaOH and precipitation by sulfuric acid. The study succeeded in extracting 90.80% silica. EDS analysis results showed that the product obtained only contains Si and O in the ratio 1:2. TEM and AFM analysis results indicated that the silica obtained has the form of nanodisk with an average diameter of 172 ( $\pm$  70) nm and the thickness of 3.09 ( $\pm$  0.74) nm. The structure of nano-disks obtained can be produced from a process that has been done is a three-stage heating, alkaline leaching, acid deposition, and freeze-drying. The surface area of the silica nanodisks obtained is 509.50 m<sup>2</sup>/g, a pore size is 5.80 nm, and a pore volume is 0.925 cm<sup>3</sup>/g.

Wattanasiriwech *et al.* in 2010 reported the results of their research on the

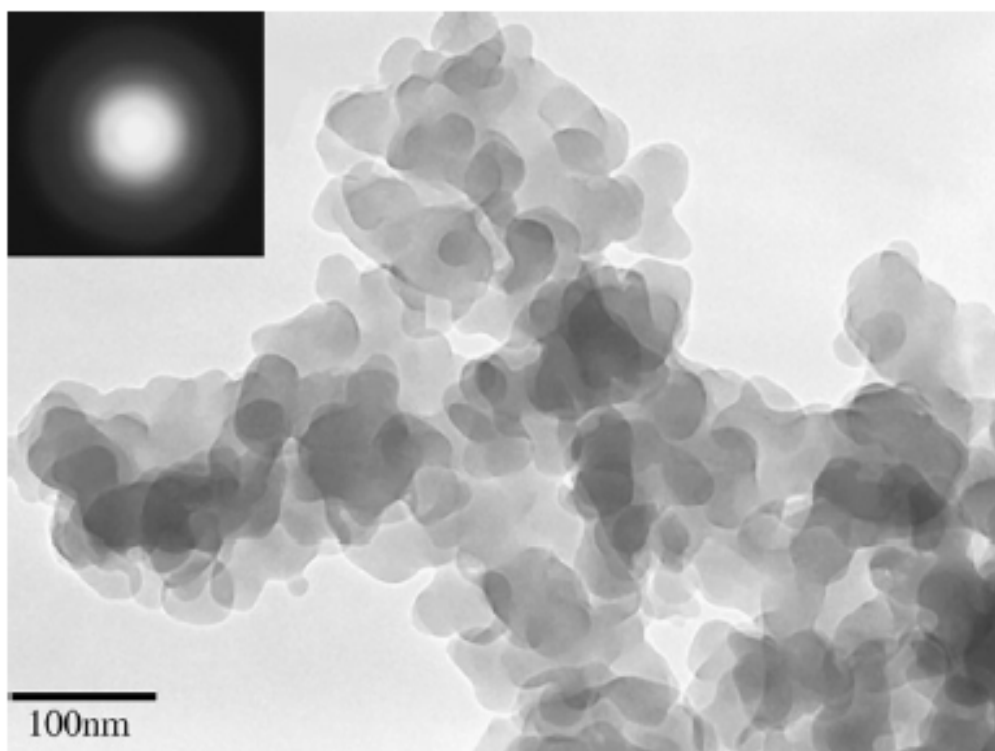
production of silica nanoparticles with microbial hydrolysis pretreatment followed by heat treatment at a temperature of 500°C for 8 hours. Microbes are from *Trichoderma reesei* TISTR 3080 and the microbial community (LDD1). The results showed that LDD1 can decompose rice straw as much as 54.80% for 72 hours while *Trichoderma reesei* (TR) can decompose as much as 40.40%. Results of hydrolysis of both microbes are shown in **Table 6**.

Calcination at a temperature of 500°C for 8 hours residues of rice straw showed that the ash derived from the residue hydrolyzed by TR is not colored white as ash produced from residues hydrolyzed by LDD1. This indicates that the ash is still contained within the carbon residue that requires a higher temperature or longer time to enhance combustion. XRF characterization results indicated that the silica content in the ash of rice straw which is hydrolyzed by TR siliceous by 82.53%, while rice straw ash that is hydrolyzed by LDD1 siliceous by 73.65% and are not hydrolysed containing silica by 72.60%. These results suggest that LDD1 is more effective to decompose rice straw compared with TR. TEM image indicated amorphous silica obtained has a particle size between 50 and 80 nm. TEM image of the silica nanoparticles were hydrolyzed by LDD1 shown in **Figure 5**.

**Table 6.** Optimal conditions of culture and hydrolysis after 72 hours of incubation. Adopted from Wattanasiriwech et al. (2010).

Culture	pH	Temperature (°C)	Weight loss (%)	Reducing sugar (g/l)	Ash content <sup>a</sup> (%)
TR	5	37	40.4 $\pm$ 0.2	0.50 $\pm$ 0.03	12
LDD1	6	40	54.8 $\pm$ 0.2	1.26 $\pm$ 0.04	23

<sup>a</sup> The values were obtained from the TGA results.



**Figure 5.** TEM picture of silica nanoparticles treated by LDD1 . Small image is SADP particles. Adopted from reference (Wattanasiriwech et al., 2010).

#### 4.3. Corn cobs

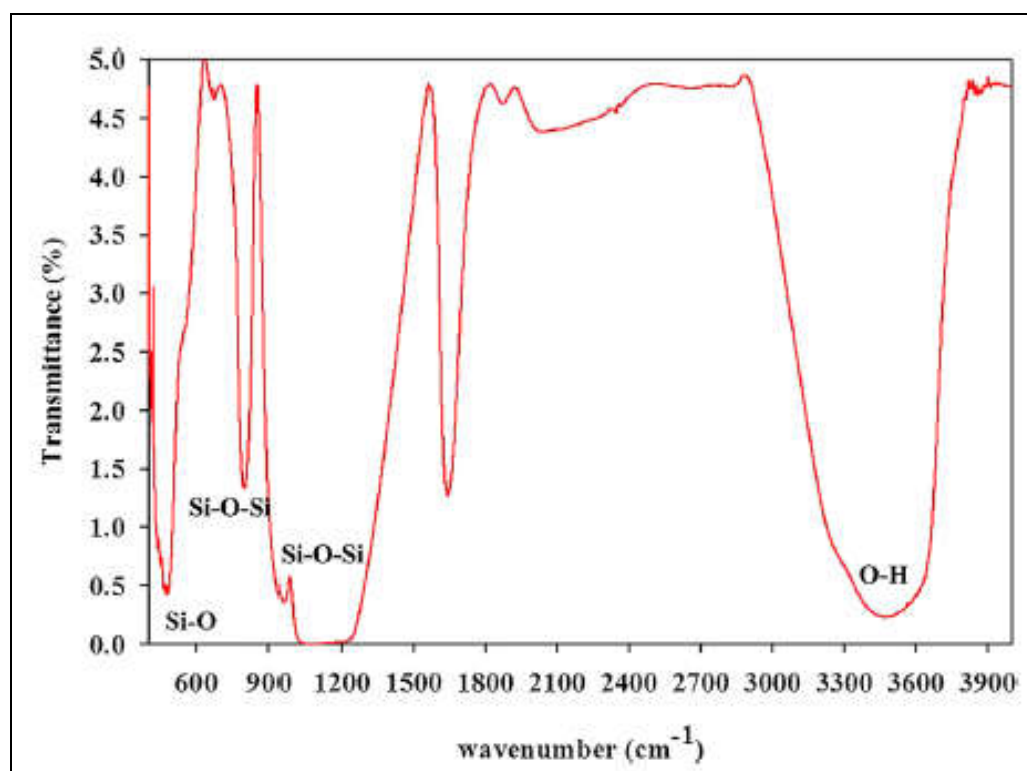
Velmurugan *et al.* isolated corn cobs using silica sol-gel method and alkali-base treatment. (Velmurugan *et al.*, 2015) From the research, amorphous silica with an average size of 50 nm can be obtained. FTIR spectra show the broad band at 3528-3596  $\text{cm}^{-1}$ , which is stretching vibration of the O-H bond from the silanol group (Si-O-Si). The band at 1050 to 1080  $\text{cm}^{-1}$  is asymmetric stretching vibration of the siloxane bonds (Si-O-Si). The band at 620-900  $\text{cm}^{-1}$  is the network Si-O-Si symmetric bond stretching vibration. The band at 469-481  $\text{cm}^{-1}$  is assigned to network O-Si-O bending vibration modes. The infrared spectroscopy (FTIR) characterization results are shown in **Figure 6**.

Shim *et al.* continued research of Velmurugan *et al.* for isolating the silica

from a corn cob with varying pH (pH 7-pH 10) using the sol - gel method. From the results, silica with a purity of 99.50%, the surface area of a large area, high reactivity, and 98.50 % amorphous was obtained. (Shim *et al.*, 2015)

#### 4.4. Bagasse

Usman *et al.* examined the silica content in the bagasse using thermal treatment with a temperature variation are at a temperature of 500, 600, and 700 $^{\circ}$ C, which ash obtained of 12.65, 10.89, and 9.95% respectively. (Usman *et al.*, 2014) XRF analysis results indicated that the levels of silica in the ash of the bagasse in a row according to the experimental temperature are 76.168, 76.292, and 77.286%.



**Figure 6.** FTIR spectra of extracted silica. Adopted from reference (Velmurugan *et al.*, 2015).

## 5. SUMMARY

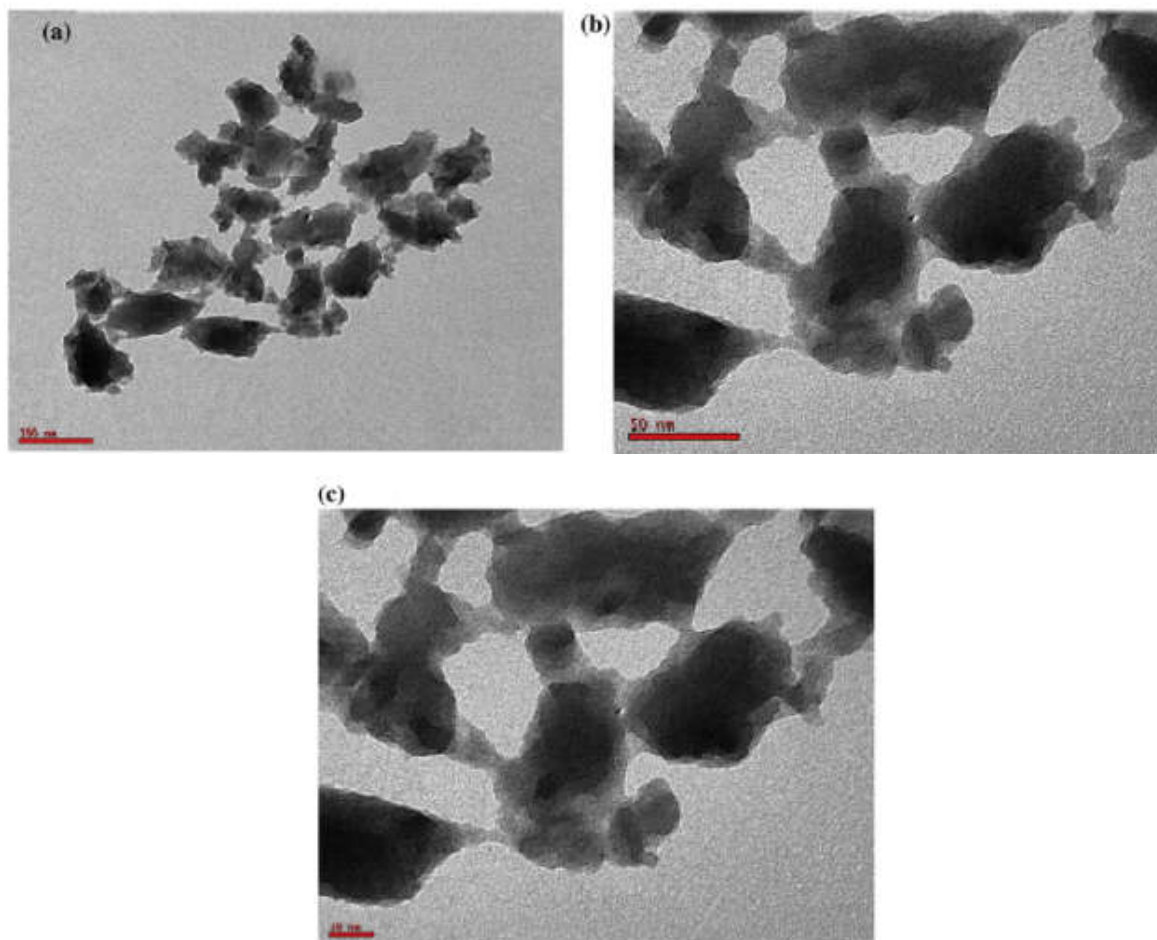
Agricultural waste such as rice husks, rice straw, corn cobs, and bagasse can be used as a source of silica. Isolation method used for extraction of silica in the agricultural waste is a chemical treatment, thermal treatment, and microbial treatment. The results showed that the agricultural waste can be used as an alternative silica source. However, this type of silica source will give advantages, not only as an inexpensive raw material but also as a problem solving to minimize the waste.

## 6. ACKNOWLEDGMENTS

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## 7. AUTHOR'S NOTES

The author(s) declare(s) that there is no conflict of interest regarding the publication of this article. Authors confirmed that the data and the paper are free of plagiarism



**Figure 7.** TEM photograph extract silica with different magnifications : (a) x100 k, (b) x50 k, and (c) x20 k. Adopted from reference (Velmurugan et al., 2015).

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