Preparation of Nanosilica from White Rice Husk Ash Powder by Precipitation Method

Noor Sarinah Mohd Noor [1], Yusnita Yaacob[2]and Erny Sabrina Mohd Noor[3]

[1]Soil Science, Water and Fertilizer Research Centre, MARDI, Headquarters Serdang, Persiaran MARDI-UPM , 43400 Serdang , Selangor, Malaysia.
[2]Business And Technology Commercialisation Centre, MARDI, Headquarters Serdang, Persiaran MARDI-UPM , 43400 Serdang , Selangor, Malaysia.
[3]Industrial Crop Research Centre, MARDI, Headquarters Serdang, Persiaran MARDI-UPM , 43400 Serdang , Selangor, Malaysia.

DOI: https://doi.org/10.56293/IJASR.2024.5910

IJASR 2024
VOLUME 7`
ISSUE 3 MAY – JUNE **ISSN: 2581-7876**

Abstract: This paper discusses the preparation and morphology of nanosilica produced from rice husk ash powder (WRHAP) by the precipitation method. There were three steps involved in the production of nanosilica from WRHAP using the precipitation method which involved extraction of silica from WRHAP, formation of silica gel and extraction of pure silica through the reflux process. The precipitation process of WRHAP was carried out using chemical treatments. The morphology of nanosilica particles observed under Transmission Electron Microscopy (TEM) showed the agglomeration of particles with spherical shape with diameters of 87 nm, 53 nm and 2 nm. The presence of siloxane bond was evident with the appearance of strong peaks in the silica nanosilica powder analysed using Fourier Transform Infra Red (FTIR). A broad peak centred at 2θ angle of 22^{o} was detected in the x-ray spectra (XRD) of nanosilica powder indicated an amorphous structure of pure silica, with the presence of small peaks due to some residues from the precipitation process.

Keywords: agriculture waste, white rice husk ash, rice husk, precipitation process, silica, microstructures

Introduction

Rice husk consists of fibrous materials with high silica content. Chemical content of rice husk consists of 46% cellulose, 26% lignin and 20% silica. Most of the weight of the harvested grains is composed of rice husk (20%). Rice husk is the result of the rice milling process and it is produced in large quantities. Various efforts have been made where the burning of the rice husk using controlled condition in the production of building materials, semiconductor and composite material (Siqueira et al. 2009). Although rice husk has many uses but it is still considered as agricultural waste that can cause pollution and disposal issues.

The type of paddy, geographical factors, soil chemical content and also the method of sample preparation will affect the chemical composition of the rice husk. Rice husk is a material that contains high level of good silica (Real et al. 1996). since then, many efforts on preparation of silica form rice husk have been conduct (Pijam et al. 2010 and Umeda et al. 2010). Recently, many have interest in using particles nano-size material which allows industries to reengineer their existing product to function at unique levels.

There are various methods on how to produced nanosilica particles from rice husk ash including direct firing under appropriate conditions, vapour phase reaction, precipitation method and enzyme treatment (Della et al. 2002; Kalapathy et al. 2000; Sun et al 2001; Wu et al. 2000; Conradt Pimkhaokham, and Leela-Adisorn 1992). Nanosilica particles could also be produced using the top down method such as grinding of wet milling technique or high pulverized mill. A combination of these methods could achieve desired size of nanosilica particles. A high surface area with lower mean particle size can be achieved following heat treatment and milling processes (Della et al. 2002). Several works had investigated the application of acid and alkaline in silica production using the chemical treatment process (Liou & Yang 2011; Chandrasekhar 2005; Chakraverty et al. 1988). This chemical treatment process is widely known as the sol gel process involves the hydrolysis and condensation of inorganic salts in the presence of mineral acids or base as a catalyst (Rahman and Padavettan 2012). The chemical treatments usually involve the pre-treatment and post-treatment processes. The purpose of pre- and post-treatment was to remove the metallic impurities, increase the surface area and produce bright white silica ash with high amount of silica content. The treatments also vary in different concentrations and treatment conditions. (Kalapathy et al. 2002) reported sodium silicate solutions were produced from rice husk ash using one molar sodium hydroxide (NaOH) solution under constant stirring at 100 °C. This sodium silicate solution was then precipitated under acidic condition to allow the gel to age.

Chakraverty et al. (1988) summarized that hydrochloric acid (HCl) was the best acid solution in removing metallic impurities in rice husk with a minimum concentration of 1 normality (N). Moreover, Chandrasekhar et al. (2005) reported that HCl was the strongest acid and most effective in removing K^+ ions and other metallic ions. Furthermore, maximum surface area of silica can be produced by HCl as reported by Liou and Yang (2011). The sodium size present in the samples were as follows; citric acids > oxalic acid > sulphuric acid (H_2SO_4) >hydrochloric acid. Generally, larger salts will be trapped in the gel matrix because of insufficient rinsing during treatment. Previous works by Liou and Wu (2010) evaluated that three molar of HCl solution and boiled at 100 °C for an hour was the best treatment to achieve high purity of silica powder from rice husk.

In addition, Conradt et al. (1992) has reported that nanostructured silica could be derived using combination of enzyme, acid pre-treatment and incineration. However, enzymatic digestion containing cellulose was only effective at the first four hours because of the growth of glucose in leachate and the solutions have to be replaced after two hours to maintain the process. Nanostructured silica also could be produced by acid leaching of rice husk prior to the combustion (Liou 2004a; 2004b). Meanwhile, nanosilica with a size of 50 nm could be obtain by the precipitation method which was reported by Thuadaij and Nuntiya (2008).

Therefore, this study was conducted to obtain the optimize condition for the preparation of purified rice husk ash, which then nanosilica will be extracted.

Materials and Methods

Raw Materials

Rice husks powder (RHP) used in this study were obtained from a rice mill in Gurun, Kedah. The rice husks were already pulverized and in a powdered form, sieved through a 150 mesh sieve using a Vibro Separator machine, which then was thoroughly cleaned using distilled water (Farook et al. 1990) and then air dried for 48 hours. Dried husk were combusted at 700 °C for 6 hours with flow a rate of 4 °C min^{-1}following the method of Della et al. (2002). The produced white rice husk ash powders (WRHAP) were used in the precipitation process to produce silica material. The lists of chemical used in the precipitation process of nanosilica were NaOH (Merck & Co), H_2SO_4 (95-98%) and HCI 36% (R & M Chemicals), with analytical grade and the solutions were prepared using distilled water.

Precipitation Process

There were three steps involved in the production of nanosilica from WRHAP using the precipitation method. Step one was the extraction of silica from WRHAP whereas step 2 involves the formation of silica gel. The final third step was the extraction of pure silica through the reflux process.

Step 1: Extraction of silica from WRHAP

The precipitation process of WRHAP was carried out using chemical treatment according to the methods of Kalapathy et al. (2000, 2002) and Thuandaij and Nuntiya (2008). NaOH solutions were used to extract pure silica from WRHAP. Modifications to the existing methods were made in the filtering process where samples were centrifuged and not filtered using a filter paper whereas a concentration of 2.0 N of NaOH solutions was used to extract pure silica from WRHAP. The solution of WRHAP were boiled for 3 hours and allowed to cool to room temperature. Using deionised water, the residues were washed and centrifuged at 3000 rpm for 15 minutes. The first reaction were as below:

$$\underset{\text{(WRHAP)}}{SiO_2} + \underset{\text{(sodium hydroxide)}}{2NaOH} \rightarrow \underset{\text{(sodium silicate)}}{Na_2SiO_3} + \underset{\text{(water)}}{H_2O}$$

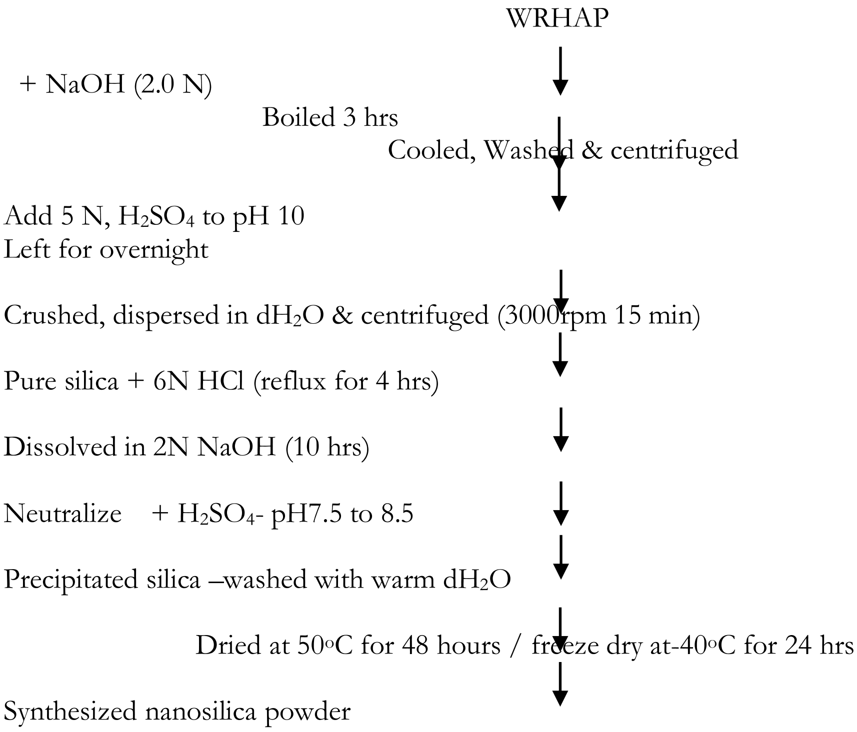
Step 2: Silica gel formation

H_2SO_4 (5.0 N) was added to the residue with constant stirring to pH 10, after which the solutions were aged overnight to allow the formation silica gel. The silica gel then crushed and dispersed in deionized water. To remove soluble salts the silica gel will centrifuged at 3000 rpm for 15 minutes. Second reaction were as shown below:

$$\underset{\text{(sodium silicate)}}{Na_2SiO_3} + \underset{\text{(sulphuric acid)}}{H_2SO_4} \rightarrow \underset{\text{(silica)}}{Si0_2} + \underset{\text{(sodium sulphate)}}{Na_2SO_4} + \underset{\text{(water)}}{H_2O}$$

Step 3: Extraction of pure silica

The method of extracting pure silica was done by reflux with HCI for 4hours, after which it was cooled and follow by washing repeatedly using deionised water. After that the extracted silica was dissolved in NaOH for 10 hours and subsequently, concentrated H_2SO_4 were added to lower the pH of about 7.5 to 8.5. Warm deionised water was used repeatedly to washed the precipitated silica and freeze-dried at -40 °C until it becomes powder. A simplified flow chart detailing the production of nanosilica using the precipitation method Kalapathy et al. (2000, 2002) is illustrated in Figure 1.



WRHAP

+ NaOH (2.0 N)

Boiled 3 hrs

Cooled, Washed & centrifuged

Add 5 N, H_2SO_4 to pH 10

Left for overnight

Crushed, dispersed in dH_2O & centrifuged (3000rpm 15 min)

Pure silica + 6N HCl (reflux for 4 hrs)

Dissolved in 2N NaOH (10 hrs)

Neutralize + H_2SO_4- pH7.5 to 8.5

Precipitated silica –washed with warm dH_2O

Dried at 50°C for 48 hours / freeze dry at-40°C for 24 hrs

Synthesized nanosilica powder

Figure 1: Production of nanosilica using the precipitation method

Characterization of Powder Materials

Nanosilica powders obtained from the precipitation process were investigated for its purity, morphological properties, particles size and physical properties. To identification the particle size of nanosilica and their structure, Transmission electron micrograph (TEM) was used (JEOL JEM-2100 electron microscope was operated at 200 kV). Nitrogen Bruner-Emmett-Teller (BET) adsorption technique in a surface area analyser (TriStar II plus, Micrometrics) was used to evaluated the specific surface area of nanosilica. Samples were degassed and vacuumed at 200°C for 24hrs. To examine any major element of silica powder, Energy Dispersive X-Ray Fluorescence (EDXRF) was used. The powder samples (5 g) were tested using fundamental parameters under air and placed under 10 mm collimator, using XRF EDX-720 spectrometer (SHIMADZU, Inc.) operated at 15 kV and 1 mA which equipped with a specialized filter which enabled the analysis at parts-per-million (ppm) levels with concentration up to 100% easily and without pre-treatment. The polymeric phases of compounds in the silica powder was identified using X-ray powder diffraction (Philips *XpertPro*) operated at 40 kV and 30 mA using Cu Kα with goniometer scan axis with a scan rate of 2^{o}C min^{-1}.

Results and Discussion

Morphological characteristics of nanosilica powder

The surface morphology of nanosilica powder is shown in Figure 2. The TEM micrograph indicated spherical particles having an average diameter of less than 100 nm. The black arrows in Figure 2 represents spherical particles with sizes of 55 nm and 2 nm, respectively. This result was in agreement with the micrographs of nanosilica powder reported by Jal et al. (2004) that observed spherical particles with a diameter of 50 nm which was uniformed and less agglomeration. Agglomeration and bi-modal distribution of microstructures were noticeable in the TEM image at higher magnification (Figure 2). The microstructure shows a fine grain of porous particles and most of the grains are estimated to have an average diameter of 2 nm with smooth edge as indicated by the black arrows. It shows that small particles have more tendencies to stack on the bigger size particles. This observation corroborates that of Thuadaij and Nuntuya (2008) who reported that rice husk nanosilica are agglomerated species within the range of 50 nm.

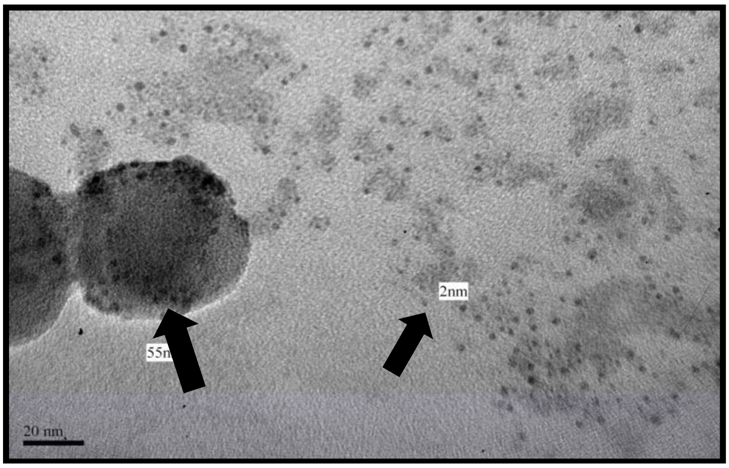


Figure 2: Transmission electron micrograph of nanosilica particles extracted from WRHAP at higher magnification (20 nm)

The formation of aggregates having particle sizes with diameters ranging below 100 nm is presented in Figure 3. The black arrows in Figure 3 showed the sticking of particles between each aggregate whereas the black arrows in Figure 4 represents the lone silica particles in spherical shape with a diameter of 87 nm.

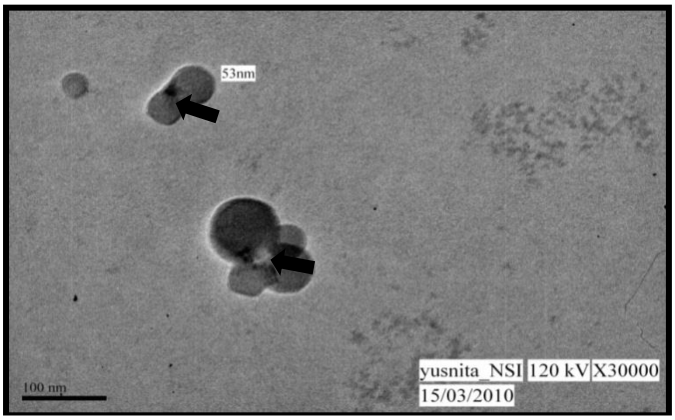


Figure 3: Transmission electron micrograph of nanosilica particles extracted from WRHAP with agglomeration

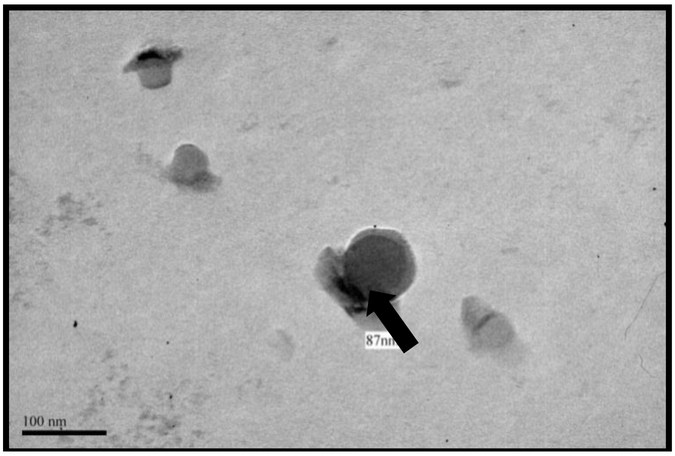


Figure 4: Transmission electron micrograph of nanosilica particles extracted from WRHAP (magnification of 100 nm)

Density and surface area of nanosilica powder

The nanosilica powder obtained from the precipitation process in this study was also determined for its density and surface area. The average densities of the nanosilica particles were 2.94 g cm^{-3}. The nanosilica density in this present study was higher compared to that reported by Jal et al. (2004) who observed an average density of 2.14 g cm^{-3}. This was due to the low content of silica which was only 60.62 %.

The BET specific surface area of nanosilica powder was found to be 18.24 m^{2}g^{-1}. Specific surface area of rice husk powder materials varies with sample treatments and processing technique. Moreover, the combustion of RHP at high temperature during the production of WRHAP contributed to increase the specific area of rice husk powder from 2.68 m^{2}g^{-1} to 12.87 m^{2}g^{-1}. This was because of the loss of cellulose, hemicellulose and lignin during the combustion process. Furthermore, the BET specific surface area will increased when the white rice husk ash samples was produces a precipitated of nanosilica powder.

The results for the BET specific surface area for the RHP, WRHAP and nanosilica powder as in Table 1. Results of specific surface area of nanosilica powder produced in this study were compared to those reported by Conradt et al. (1992), Yalcin and Sevinc (2001) and Jal et al. (2004). The specific surface area of NSI in this present study was lower than the reported range as specific surface areas of 560 m^{2}g^{-1}, 200 to 250 m^{2}g^{-1}, and 200 to 300 m^{2}g^{-1} were reported by Jal et al. (2004), Conradt et al. (1992), and Yalcin and Sevinc (2001), respectively. The specific surface are of RHP was lower than WRHAP and nanosilica powder. This could be ascribed to the agglomeration effects and pulverization of RHP at the rice mill factory that contributed to less porosity in sample of rice husk (Della et al. 2002). The irregularities of the size was distribution and agglomeration from treatments effects might have caused the compaction of pores that resulted in low specific area.

Table 1: Specific surface area, pore volume and average pore diameter for RHP, WHRAP, and nanosilica powder

Sample	Specific surface area (m^{2}g^{-1})	Pore volume (ccg^{-1})	Average pore diameter (A)
RHP	2.68	0.0079	25.35
WRHAP	12.87	0.0772	35.22
NSI	18.24	0.1483	17.64

Elemental composition of nanosilica powder

The elemental composition was carried out to measure the percentage of silica content in the sample before and after treatment. The elemental composition of RHP, WRHAP, and nanosilica powder is shown in Table 2. The content of silica in RHP was 58.84% but the concentration decreased to 56.70% in WRHAP, after which the silica increased to 60.62% in nanosilica powder. This result also corroborates that of Carmona et al. (2013) who reported an increased in Si content after the precipitation method was carried out.

This is due to the chemical treatment that purified the silica content in the rice husk. The chemical process involved in the precipitation method eliminated the carbon residue and other traces.

The silica content in NSI was higher than that reported by Carmona et al. (2013) who observed silica content ranging between 31 to 35%. However, the silica content in NSI was lower compared with those reported by Yalcin and Sevinc (2001) and Conradt et al. (2002). The silica content reported by Yalcin and Sevince (2001) and Conradt et al. (2002) were within the range of 91 to 99%. Moreover, they observed that rice husk sample treated with NaOH contributed to lower silica content ranging between 39.80 to 68.3%.

Table 2. Elemental composition of RHP, WRHAP and nanosilica powder

Properties	RHP	WRHAP	Nanosilica powder
	Concentration (%)		
Silica	58.84	56.70	60.62
Potassium	28.38	27.54	24.08
Calcium	6.11	7.35	6.07
Sulphur	3.02	3.32	4.15
Iron	1.51	2.75	1.88
Copper	0.41	0.35	0.25
Magnesium	1.43	1.46	1.06
Zinc	0.29	0.40	0.28

Molecular structure of nanosilica powder

A broad peak in the range of 18 to 30o (2θ) result form x-ray spectra of nanosilica powder indicated an amorphous structure of pure silica which is marked as black circle in Figure 5. This result corroborates that of Kalapathy et al. (2002) who also observed the same broad peak centred at 2*θ* angle of 22°, with presence of small peak due to some residues of other elements from the precipitation process.

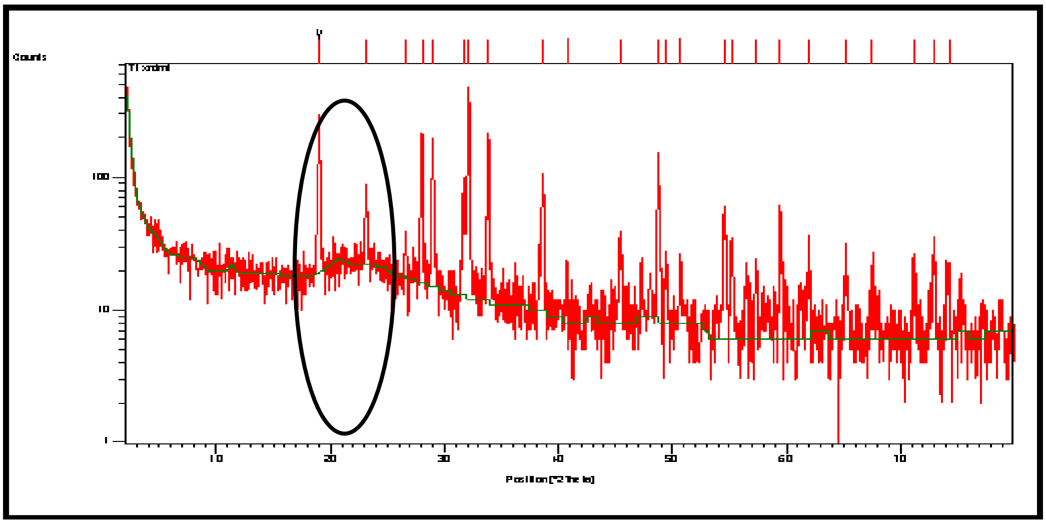


Figure 5: X-ray diffraction spectrum of nanosilica powder

Functional groups of nanosilica powder

The infrared spectrum of RHP, WRAP, and nanosilica powder is presented in Figure 6. The functional groups in RHP, WRAP, and nanosilica powder were identified based on the following major peaks at different wavelengths: 3448 cm^{-1} , 3394 cm^{-1}, 2928 cm^{-1}, 2361 cm^{-1}, 1648 cm^{-1}, 1112 cm^{-1} ,1103 cm^{-1}, 803 cm^{-1}, 616 cm^{-1}, 471 cm^{-1}. A broad peak in the range of 3394 cm-1 and 3448 cm-1 respectively, indicate the stretching vibration of the O-H bond. this peak indicated the present of silanol OH groups and the adsorbed water bound to the silica surface. However, there were no broad peaks detected at the range of 3400 cm^{-1} in WRHAP. This could be attributed to the loss of the OH group during the combustion process (Ibrahim 1980a).

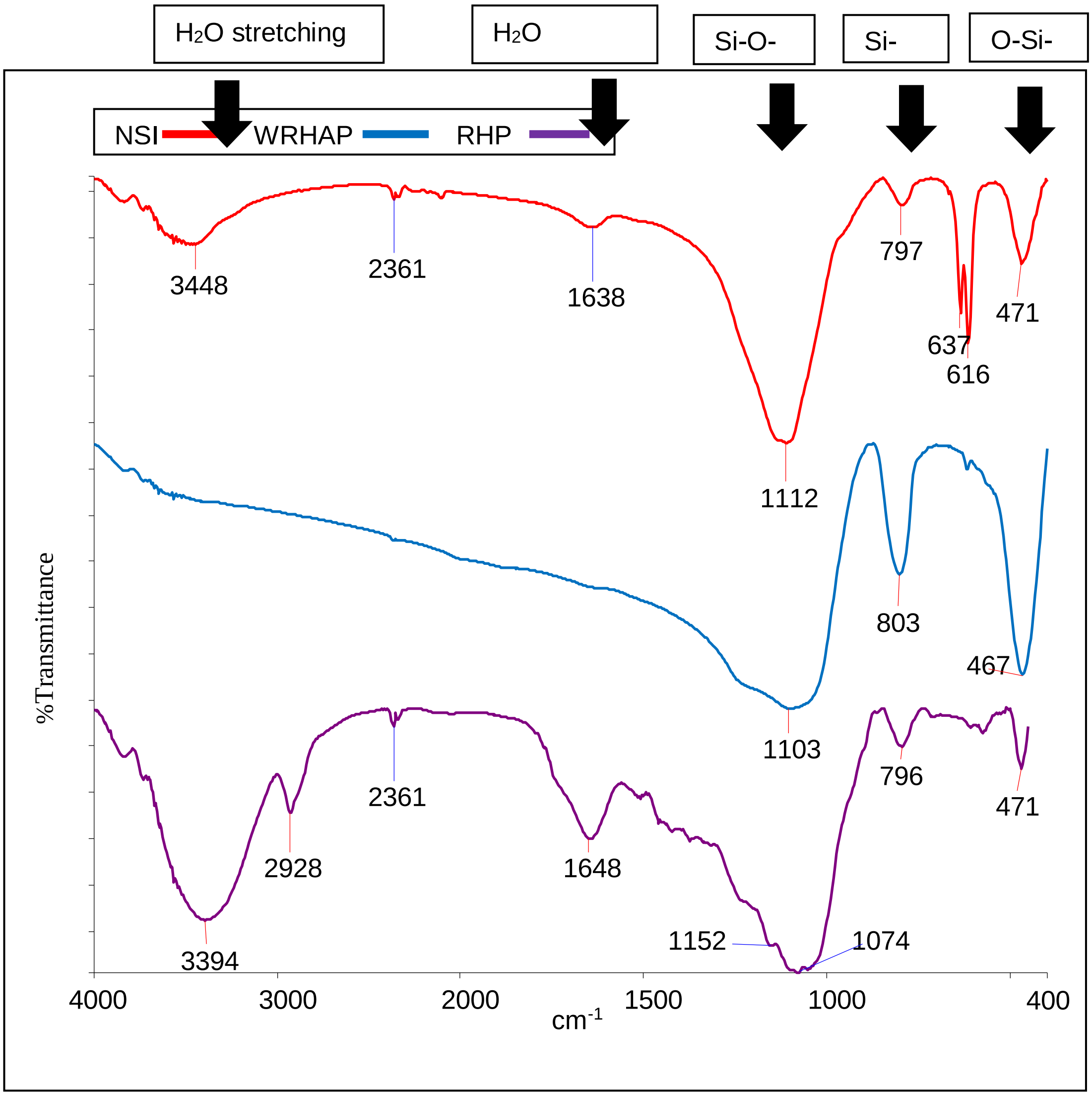


Figure 6: Infrared spectrum of nanosilica powder, WRHAP, and RHP

The bending vibrations for RHP and nanosilica powder occurred at wavelengths of 1648 cm^{-1} and 1638 cm^{-1}, respectively. These bending vibrations could be attributed to water molecules that were trapped in the matrix of silica (Jal et al. 2004). Although these bending vibration peaks were present in RHP and nanosilica powder, they were absent in the WRHAP samples due to the loss of OH groups during the combustion process.

The infrared spectrum showed strong peaks at 1100 cm-1 to 1075 cm-1. The structural of siloxane bond (Si-O-Si) which is related with this peaks. The shifting of the peak from 1152 cm-1 to 1074 cm-1 is caused to the asymmetric stretching of the Si-O-Si in the tetrahedrons structure. This peak was present in the infrared spectrum in the nanosilica powder, WRHAP, and RHP samples. The peaks occurring at wavelengths of 803 cm-1, 797 cm-1, 637 cm-1 and 616 cm-1 are due to the OH bending of silanol group. This result corroborates that of Liou and Yang (2011). Moreover, the sharp peaks at 637 cm-1 and 616 cm-1 in the nanosilica powder sample indicates the presence of silica because of the compact agglomeration of silica particles which increase the strength of hydrogen bonding between intermolecular in the gelation reaction.

Conclusion

Precipitation process of WRHAP using simple chemical treatment successfully produces nanosilica particles in the range of 87 nm, 53nm and 2nm. Spherical shape particles with agglomeration were evidenced having 60.62% purity and 18.24 m^2g^{-1} specific surface areas. This study shows that by using chemical treatment methods, rice mill operators can produce nanosilica, which can reduce the burning of rice husk and thus reduce the impact on the environment.

References

1. Carmona, V. B., Oliveira, R. M., Silva, W. T. L, Mattoso, L. H. C. and Marconcini, J. M. (2013). Nanosilica from rice husk: Extraction and characterization. *Industrial Crops and Products* 43: 291-296
2. Chandrasekhar, S., Pramada, P.N. and Praveen, L. (2005). Effect of organic acid treatment on the properties of rice husk silica. *Journal of Materials Science*, 40, 6535–6544
3. Chakraverty, A., Banerjee, H.D., & Pandey, S.K. (1988). Studies on thermal decomposition of rice straw. *Thermochimica Acta,* 120, 241-255
4. Conradt, R., Pimkhaokham, P., & Leela-Adisorn U. (1992). Nano-structured silica from rice husk. *Journal Non-crystalline Solids,* 145, 75-79
5. Della, V.P., Kuhn, I., & Hotza, D. (2002). Rice husk ash as an alternate source for active silica production. *Journal Material Letters,* 57, 818-821
6. Farook, A., Ismail, A. R., & Muhammad, I. S. (1990). Production and characterization of rice husk ash as a source of pure silica, *J. Seramik*, 89, 261-273
7. Ibrahim, D.M., El-Hemaly, S.A., & Abdel-Kerim, (1980a). Study of rice husk ash silica by infrared spectroscopy. *J. Thermochimica Acta,* 37, 307-314
8. Jal, P.K., Sudarshan, M., Saha, A., Patel, S., Mishra, B.K. (2004). Synthesis and characterization of nanosilica by precipitation method. J. *Colloids and Surfaces A: Physicochem. Eng. Aspects,* 240, 173-178
9. Kalapathy, U., Proctor, A., Shultz, J. (2000) A simple method for production of pure silica from rice hull ash. *J. Bioresource Technology* 73, 257-262
10. Kalapathy, U., Proctor, A., Shultz, J. (2002) An improved method for production of silica from rice hull ash. *J. Bioresource Technology* 85, 285–289
11. Liou, T.-H., & Yang, C.-C. (2011). Synthesis and surface characteristics of nanosilica produced from alkali-extracted rice husk ash. *J. Materials Science and Engineering: B,* 176(7), 521-529.
12. Liou, T.-H., (2004a). Preparation and characterization of nano-structured silica from rice husk. *J. Materials Science and Engineering: A,* 364(1-2), 313-323
13. Liou, T-H. (2004b). Evolution of chemistry and morphology during the carbonization and combustion of rice husk. *J. Carbon,* 42, 785-794
14. Pijam, N., Taroenworaluch, A., Sunsaneeyametha, W., Stevens, R. (2010). Synthesis and characterization of nanosized silica gels formed under controlled conditions. *Powder Technology*. 203 (3): 462-468
15. Rahman, I.A. and Padavettan, V. (2012) Synthesis of Silica Nanoparticles by Sol-Gel: Size-Dependent Properties, Surface Modification, and Applications in Silica-Polymer Nanocomposites—A Review. *Journal of Nanomaterials*, 1-15
16. Real, C.,Alcala, M.D.,Criado, J.M. (1996). Preparation of silica from rice husks. *J.Am.Ceram.Soc.*79, 2012-2016
17. Siqueira, E.J.,Yoshida, M.P.,Pardini,L.C.,Schiaven, M.A.(2009). Preparation and Characterization of ceramic compisites derived from rice husk ash and polysiloxane, *Ceramics International*,35,213
18. Sun, L., Gong, K. (2001). Silicon –based materials from rice husk and their application. *Ind. Eng. Chem. Res.* 40, 5861
19. Thuadaij, N.,& Nuntiya, A. (2008). Preparation of Nanosilica Powder from Rice Husk Ash by Precipitation Method. *Chiang Mai J. Sci*. 35(1), 206-211

20. Umeda, J., Kondoh, K. (2010). High purification of amorphous silica originated from husks by combination of polysaccharide hydrolysis and metallic impurities removal. *Ind. Crop. Prod.* 32, 539
21. Wu, G., Wang, J., Shen, J., Yang,T.,Zhang, Q., Zhou, B., Beng, Z., Bin, F., Zhou, D., Zhang, F. (2000). Properties of sol-gel derived scratch-resistant nano-porous, silica films by a mixed atmosphere treatment. *J. non-cryst. Solids.* 275,167
22. Yalcin, N. and Sevinc, V. (2001). Studies on Silica Obtained from Rice Husk. *Ceramics International*, 27, 219-224.