A Simple Method for the Production of Pure Crystalline Silica from Lemon Grass

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Lemon grass is an inexpensive raw material that can be used to produce natural silica. A method using hydrochloric acid (HCl) leaching followed by thermal combustion at 600 °C was developed to produce purified silica from lemon grass. Acid leaching temperatures of 33, 50, 80, and 110 °C were used. The silica content of the lemon grass ash was characterized using X-ray fluorescence (XRF), X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) analysis. The shape and texture of the lemon grass ash were studied using SEM. The highest silica content (98.59%) was produced by lemon grass that had been treated at the highest leaching temperature (110 °C). Other elements that were found in the lemon grass ash were magnesium, calcium, potassium, and chlorine. XRD analysis showed that the crystallinity of the silica in treated lemon grass ash increased with increasing leaching temperature. The FTIR analysis confirmed the presence of siloxane and silanol bonds in lemon grass that was calcined at different leaching temperatures.

Keywords: Silica; Inorganic compounds; Acid leaching treatment; Crystallinity

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INTRODUCTION

Silicon dioxide (SiO_2) or silica is a mineral that is widely used in ceramics, adhesives, composites, detergents, and pharmaceutical products. It is also a major precursor for various types of inorganic and organometallic materials (Okoronkwo *et al.* 2013; Terzioglu *et al.* 2013). Generally, commercial silica is produced from the fusion of high purity caustic soda with silica sand in a furnace at a temperature range from 1300 to 1500 °C. The most common commercial silica precursor, which is used in the plastics industry, is tetraethylorthosilicate (TEOS). However, the manufacturing process is very expensive and consumes a high amount of energy (Srivastava *et al.* 2013). Table 1 indicates the applications of silica in various industries.

Silica is precipitated from various types of bio waste, such as rice husk, bagasse, rice hull, and lemon grass. Silica is the predominant mineral in the ash of perennial grasses (Samson and Mehdi 1998). The presence of silica in perennial grasses depends on the amount of silicic acid in the water absorbed by the roots and on photosynthesis. Moreover, the silica level is higher in inflorescences, leaves, and leaf sheathes than in the stem fraction of the grasses. Silica found in the grasses can be obtained from heating the grasses to an elevated temperature to remove carbon and other volatiles (Onojah *et al.* 2012). There are many silica extraction techniques including acid leaching and gasification. Leaching extracts solid materials into liquid form or removes impurities from solid materials. Sulphuric (H_2SO_4), hydrochloric (HCl), and nitric (HNO_3) acids are conventionally used in the leaching process (Umeda and Katsuyoshi 2008). Acid leaching removes most metals and increases the specific surface area of the grass ash (Olawale and Oyawale 2012). The acid leaching of lemon grass before combustion results in a higher purity of silica (Umeda *et al.* 2007).

Cymbopogon citratus (lemon grass) is perennial grass, which is cultivated in tropical and subtropical countries such as South Africa, Sri Lanka, Indonesia, Thailand, and Malaysia (Nambiar and Matela 2012).The most effective temperature for lemon grass cultivation is within a range from 18 to 29 °C, with a soil pH ranging from 5.0 to 5.8 (Punam *et al*. 2012). According to Oloyede (2009), lemon grass consists of crude protein, ash, crude fiber, fat, carbohydrates, and minerals. Proximate analysis shows that this plant has a high carbohydrate content (38.44%), ash content (13.43%), and many important minerals such as silica (9.02%), phosphorous (1.57%), potassium (54.02%), and calcium (25.87%). However, the observed mineral content varies with different methods of sample preparation and testing. Ogie-Odia *et al.* (2010) studied the epidermal and phytochemical features of lemon grass using a scanning electron microscope. The micrograph showed the presence of silica bodies, mostly in a cross shape on the adaxial surface of the lemon grass. This micrograph revealed the presence of silica content in lemon grass ash, which can be extracted as a replacement for commercial silica. In this study, crystalline silica was prepared from lemon grass using an acid leaching treatment.

Table 1. Application of Silica in Various Industries

Type of application	Silica function
Polymer Composite	- Reinforcement material - Catalyst
Rubber	- Reinforcement material - Extending agent - Colouring agent
Glass and ceramic	- Filler
Pharmaceutical products	- Filler - Release carrier - catalyst
Adhesives	- Reinforcement material - Fire retardant

* Okoronkwo *et al.* (2013); Terzioglu *et al.* (2013); Srivastava *et al.* (2013)

EXPERIMENTAL

Materials

Lemon grass was obtained from Stesen Agroteks UniMAP, Perlis, Malaysia. This lemon grass was cultivated on heavy clay soil that has a high silica content. The raw material was ground, sieved, and dried before undergoing the treatment process. Hydrochloric acid (HCl, 37%) was used for the acid leaching treatment and was supplied by AR Alatan Sdn Bhd, Kedah, Malaysia.

Acid Leaching Treatment

Lemon grass was soaked in 5M HCl for 3 h at 33 °C, 50 °C, 80 °C, or 110 °C. Treated lemon grass was rinsed with warm distilled water and dried overnight in an oven at 105 °C. Dried lemon grass was calcined at 600 °C until it became white ash.

Silica Characterization

The silica and other metallic element contents in the sample was investigated by X-ray fluorescence (XRF) with a PANanalytical MiniPAL 4 x-ray spectrometer (Philips, UK). Phase identification of extracted silica was determined by X-ray powder diffraction (XRD) using a Bruker D2 phaser X-ray diffractometer, with a Cu-Kα1 radiation of λ= 1.54 Å, generator tension of 30 kV, a generator current of 10 mA in the 2θ range of 10° to 80° and a rate of 2°/min. The crystallinity index (CI) was calculated by EVA software using the XRD intensity data obtained by the peak deconvulation method. Individual crystal peaks were extracted by curve-fitting from the diffraction intensity profiles using a peak fitting program, with assumed Gaussion functions for each peak (Saceda and De Leon 2011). CI was calculated using Eq. 1,

$$\text{CI (\%)} = \left(\frac{A_{cr}}{A_{total}}\right)(100) \tag{1}$$

where A_{cr} is the area of all crystallinity peaks and A_{total} is the total area.

Scanning electron microscopy (SEM) was carried out using a computer-controlled field emission SEM (model JSM 6460 LA, JEOL, USA). To identify the types of chemical bonds (functional groups), the diffuse reflectance Fourier transform infrared spectroscopy (FTIR) technique was performed for all samples with a spectrometer (model L1280044, Perkin Elmer, USA). All spectra were scanned 4 times in the range of 4000 to 400 cm^{-1}, with a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

X-Ray Fluorescence Analysis

Table 2 shows the chemical composition of non-treated lemon grass and treated lemon grass ash that were leached at different temperatures. Non-treated lemon grass recorded the lowest silica content. Moreover, the silica content of treated lemon grass increased as the leaching temperature increased. The highest silica content, 98.59%, was recorded for lemon grass ash treated at the highest leaching temperature of 110 °C.

Table 2. Chemical Composition of Lemon Grass Treated at Different Temperatures and Calcined at 600 °C

Components	Non-Treated Lemon Grass (%)	37 °C (%)	50 °C (%)	80 °C (%)	110 °C (%)
SiO_2	10.9	67.06	74.12	95.95	98.59
MgO	2.0	-	-	-	-
K_2O	47.27	1.72	1.07	0.31	0.17
CaO	25.3	16.5	0.58	0.57	0.22
Fe_2O_3	0.29	0.08	0.13	0.31	0.33
P_2O_5	3.91	-	-	-	-

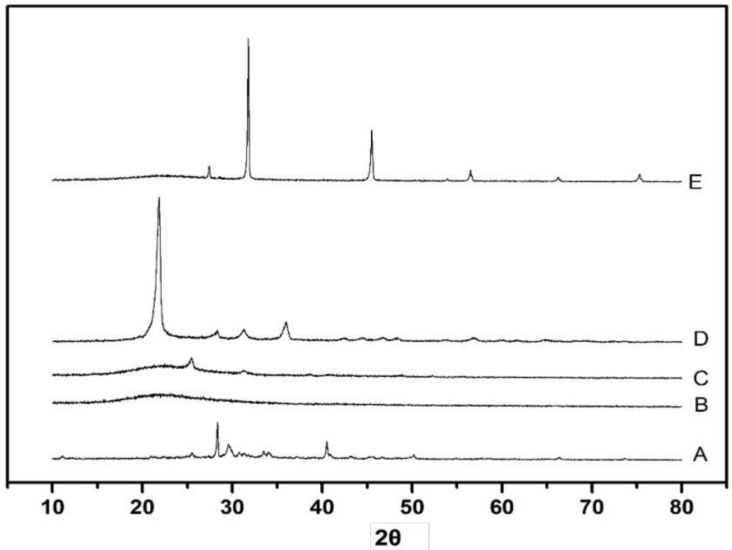

Fig. 1. X-ray diffractograms of ash from (A) untreated lemon grass and lemon grass leached at (B) 33 °C, (C) 50 °C, (D) 80 °C, and (E) 110 °C

X-Ray Powder Diffraction

X-ray diffractograms were recorded from the ash of raw lemon grass and lemon grass treated at different leaching temperatures (Fig. 1). Non-treated lemon grass calcined at 600 °C exhibited sharp crystallinity peaks at 2θ values of 28.6°, 29.7°, 33.4°, 41.1°, and 50.2° (Fig. 1A). These peaks indicated *d*-values of 3.11, 3.00, 2.67, 2.19, and 1.81 respectively.

As previously observed (Rahman *et al.* 2009), the XRD patterns of treated lemon grass ash at different leaching temperatures had many sharp peaks in crystallinity (Fig. 1B). Lemon grass leached at 33 °C contained amorphous materials, which are represented by the peak at 22°. The sharpest peaks at 27.4°, 32.8°, 45.5°, 56.7°, and 66.8° were obtained after leaching at 110 °C (Fig. 1D). These peaks resulted in d-values of 3.24, 2.72, 2.85, 1.66, and 1.45, respectively, from the Bragg's equation calculation (Saceda and De Leon 2011).

The crystallinity of lemon grass silica increased as the acid leaching temperatures increased (Table 3), as impurities in the lemon grass ash were removed (Umeda and Katsuyoshi 2008). Lemon grass that was leached at 110 °C had the highest crystallinity degree (72.90%). However, the degree of crystallinity for non-treated lemon grass calcined at 600 °C was higher than lemon grass leached at lower temperatures.

Table 3. Crystallinity Index of Different Temperatures of Treated Lemon Grass Calcinated at 600 °C Temperature

Acid Leaching temperatures (°C)	Crystalline Structure (%)	Amorphous Structure (%)
0 (No Treatment)	55.00	45.00
37	31.30	68.70
50	33.40	66.60
80	50.60	49.40
110	72.90	27.10

Silica crystallization usually occurs during the heating process; amorphous silica converts to crystalline silica as the temperature is increased (Umeda *et al.* 2007). Therefore, the temperature of the acid leaching treatment can control the degree of silica crystallization. Acid leaching removes metal elements such as potassium (K) and sodium (Na) that form crystalline structures with silica at high temperatures. The removal of these impurities is crucial for recovering amorphous silica (Mehdi *et al.* 2009).

Fourier Transform Infrared Analysis

FTIR spectroscopy was conducted to study the functional groups in treated lemon grass (Fig. 2A, B, C, D, and E). The peaks from 3300 to 3200 cm^{-1} corresponded to the stretching vibrations of Si-OH or H-OH. Lemon grass fiber is hydrophilic in nature; therefore, the hydroxyl group present in the cell wall structure of the lemon grass forms hydrogen bonds with water molecules (Khemthong *et al.* 2007).

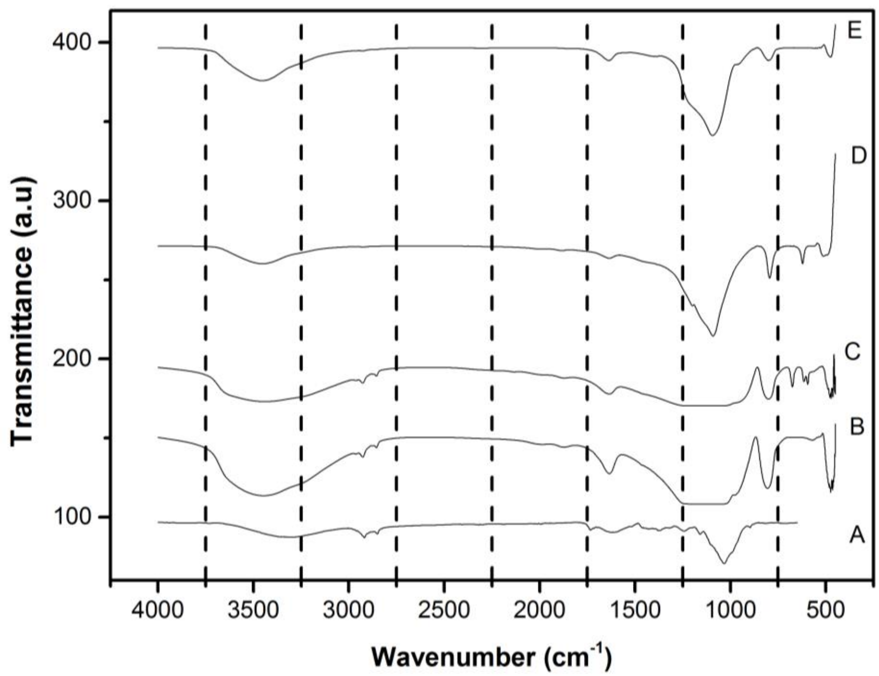

Fig. 2. FTIR spectra of ash from(A) untreated lemon grass and lemon grass leached at (B) 33 °C, (C) 50 °C, (D) 80 °C, and(E) 110 °C

The peaks from 3000 to 2800 cm^{-1} showed the stretching of Si-H bonds, and they were not found in lemon grass leached at higher temperatures. According to Rafiee and Shahebrahimi (2012), no original organic compounds are present in treated lemon grass ash after controlled combustion and extraction. The strongest broad IR band was recorded between 1200 cm^{-1} and 1000 cm^{-1} (Table 4). This range is usually assigned to asymmetry between Si-O and Si-O-Si bonds (Nayak and Bera 2009), whereas peaks from 800 to 700 cm^{-1} are due to the symmetric stretching mode of the Si-O-Si bond. The band from 450 to 600 cm^{-1} corresponds to the Si-O-Si bending vibration. However, there was no peak recorded at 600 to 450 cm^{-1} in non-treated lemon grass (Haslinawati *et al.* 2009). This result was due to the removal of a metal element that improves the purity of lemon grass silica (Khemthong *et al.* 2007).

Table 4. Infrared Spectra of Lemon Grass Leached at Different Temperatures

Wavenumber (cm^{-1})					
Vibrational Band Assignment	Non-Treated	37 °C	50 °C	80 °C	110 °C
Si-OH or H-OH Stretching	3055 1405 -	3445 1870 1634	3446 1871 1635	3458 - 1636	3458 - 1637
Si-H Stretching	- - -	2926 2855 -	2961 2926 2854	- - -	- - -
Si-O-Si Asymmetric Stretching	-	1128	1136	1091	1092
Si-O-Si Symmetric Stretching	872 709	805	800	794	793
Si-O-Si Bending	-	- 567 467	614 594 462	621 511 -	- - 476

Scanning Electron Microscopy

The morphology of ash from lemon grass treated at different reaction temperatures is presented in Figs. 3 to 7. Figure 3 shows the non-treated lemon grass ash calcined at 600 °C. Non-treated lemon grass ash exhibited fibrillar structure and more tubular-shaped porous aggregates. These characteristics are due to the higher content of magnesium (Mg) and potassium (Borlini *et al.* 2008).

As observed in Figs. 4, 5, 6, and 7, various sizes and geometry—tubular-shaped porous aggregates and spherical or and fibrous particles—were present in treated lemon grass. More spherical particles were present in the treated lemon grass at the acid leaching temperatures of 80 °C and 110 °C. The agglomeration of ash structures also increased as the temperature increased because of the increasing crystalline structure. The spherical particles contain mostly silica (Si) but also sodium (Na), potassium (K), aluminium (Al), ferum (Fe), magnesium (Mg), and calcium (Ca) (Hariharan and Sivakumar 2013).

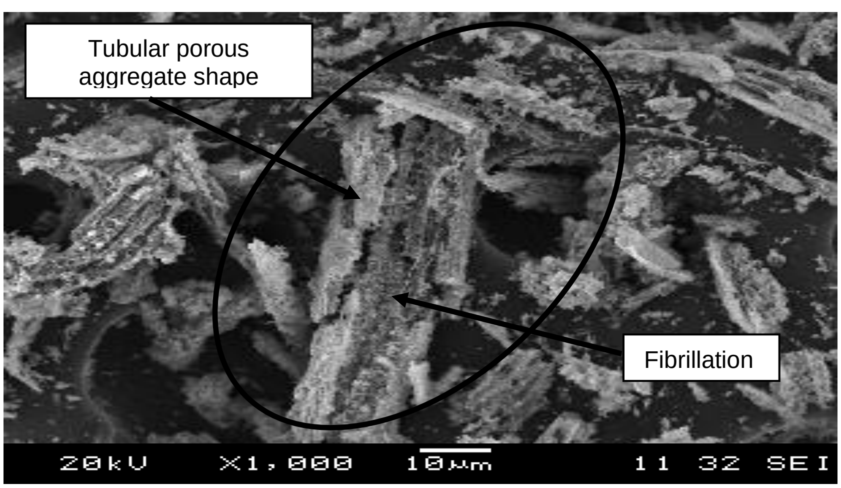

Fig. 3. SEM micrograph of non-treated lemon grass calcined at 600 °C

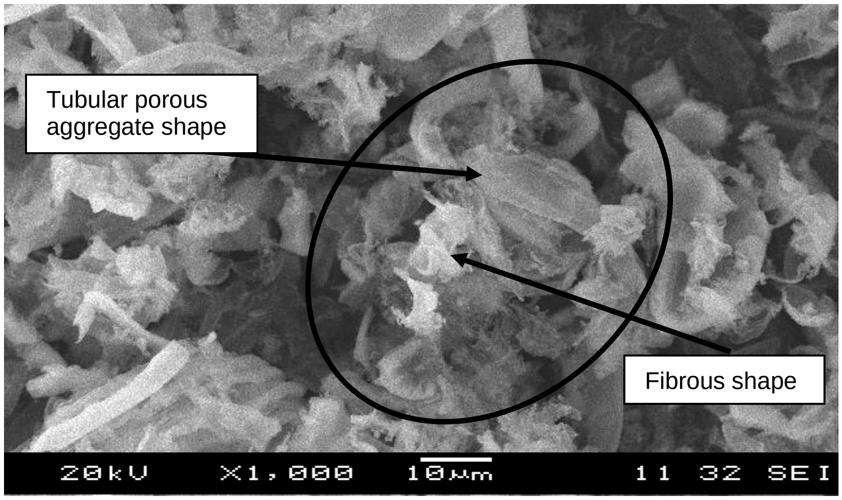

Fig. 4. SEM of treated lemon grass leached at 37 °C and calcined at 600 °C

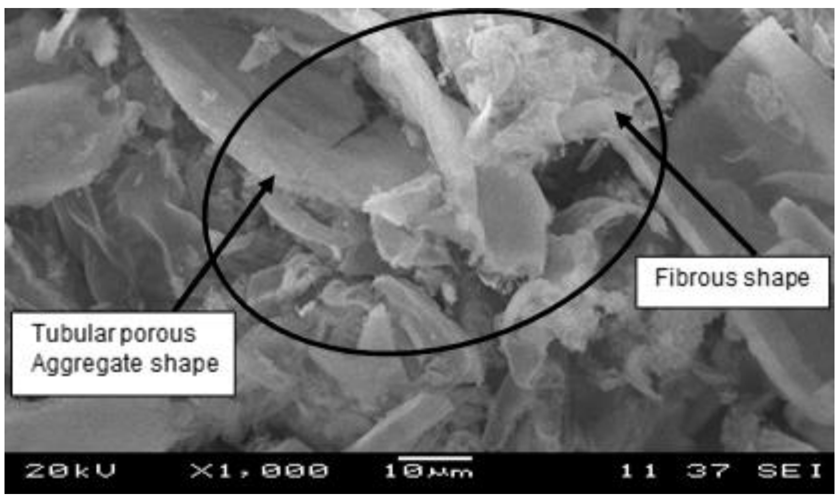

Fig. 5. SEM of treated lemon grass leached at 50 °C and calcined at 600 °C

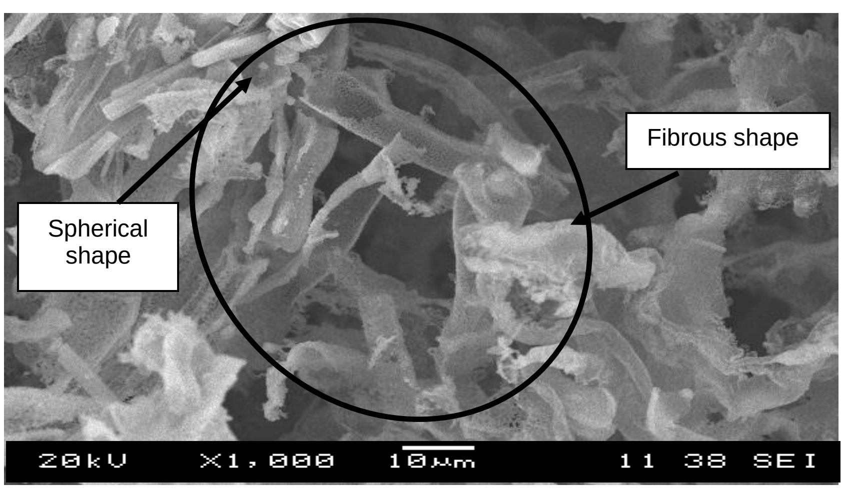

Fig. 6. SEM of treated lemon grass leached at 80 °C and calcined at 600 °C

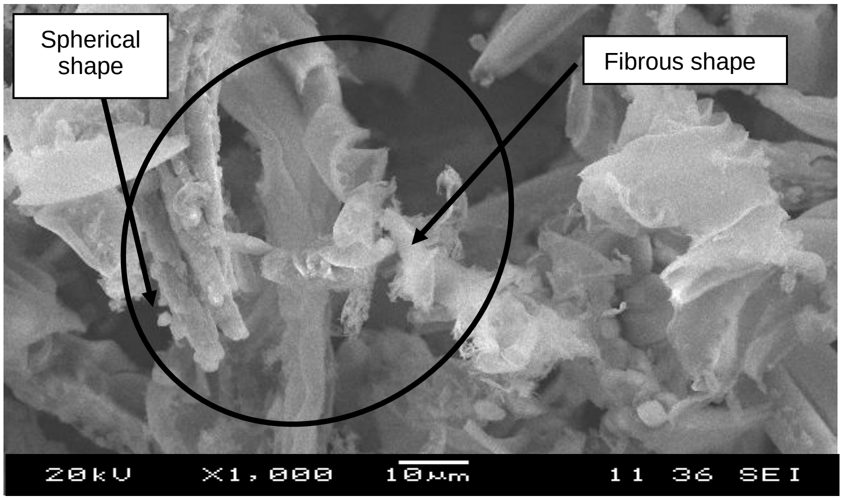

Fig. 7. SEM of treated lemon grass leached at 110 °C and calcined at 600 °C

CONCLUSIONS

1. Silica from treated lemon grass ash was obtained at a calcination temperature of 600 °C. The highest value of silica content (98.58%) was recorded at a leaching temperature of 110 °C.
2. The crystallinity degree of silica in lemon grass ash increased from 55% to 62.9% as the leaching temperature increased from 33 °C to 110 °C.
3. FTIR analysis showed the presence of siloxane (Si-O-Si) and silanol (Si-OH) groups in the lemon grass ash as the leaching temperature increased from 33 °C to 110 °C.
4. SEM analysis showed the presence of tubular-shaped porous aggregates as well as spherical and fibrous particles in lemon grass treated at 33 °C to 110 °C.

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REFERENCES CITED

Borlini, M. C., Vieira, C. M. F., Sanchez, R., Contez, R. A., Pinatti, D. G., and Monteiro, S. N. (2008). "Characterization of granulometric fractions of ash from boiler burnt sugarcane bagasse," *Materials Science Forum* 591-593, 471-476. DOI: 10.4028/www.scientific.net/MSF.591-593.471

Hariharan, V., and Sivakumar, G. (2013). "Studies on synthesized nanosilica obtained from bagasse ash," *International Journal of Chemical Technology and Research* 5(2), 1263-1266.

Haslinawati, M. M., Matori, K. A., Wahab, Z. A., Sidek, H. A. A., and Zainal, A. T. (2009). "Effect of temperature on ceramic from rice husk ash," *International Journal of Basic & Applied Sciences* 9(9), 22-25.

Khemthong, P., Pryoonpokarach, S., and Wittayakun, J. (2007). "Synthesis and characterization of zeolite lsx from rice husk silica," *Journal of Science and Technology* 14(4), 367-379.

Mehdi, J., Jalaludin, H., Alireza, S., Manjusri, M., and Kristiina, O. (2009) "Chemical composition, crystallinity, and thermal degradation of bleached and unbleached kenaf bast (*Hibiscus cannabinus)* pulp and nanofibers," *BioResources* 4(2), 626-639.

Nambiar, V. S., and Matela, H. (2012). "Potential functions of lemon grass (*Cymbopogon citratus*) in health and disease," *International Journal of Pharmaceutical and Biological Archives* 3(5), 1035-1043.

Nayak, J., and Bera, J., (2009). "A simple method for production of humidity indicating silica gel from rice husk ash," *Journal of Metals, Materials and Minerals* 19(2), 15-19.

Ogie-odia, E. A., Eseigbe, D., Ilechie, M. N., Erhabor, J., and Ogbebor, E. (2010). "Foliar epidermal and phytochemical studies of the grasses *Cymbopogon citratus* (Stapf.), *Axonopus compressus* (P. Beauv.) and *Eragrostis tremula* (S. W. Beauv) in Ekpoma, Edo State, Nigeria," *Science World Journal* 5(4), 20-25. DOI: 10.4314/swj.v5i1.61481

Okoronkwo, E. A., Imoisili, P. E., and Olusunle, S. O. O. (2013). "Extraction and characterization of amorphous silica from corn cob ash by sol-gel-method," *Chemistry Materials Research* 3(4), 68-72. DOI: 10.1016/j.jiec.2015.05.029

Olawale, O., and Oyawale, F. A. (2012). "Characterization of rice husk via atomic absorption spectrophotometer for optimal silica production," *International Journal of Science and Technology* 2(4), 210-213. DOI: 10.1.1.301.1849

Oloyede, O. I. (2009). "Chemical profile and antimicrobial activity of *Cymbopogon citratus* leaves," *Journal of Natural Products* 2(3), 98-103.

Onojah, A., Amah, A. N., and Echi, I. M. (2012). "Polymorphs of crystalline silica from rice husk ash," *Journal of Basic Physical Research* 3(2), 73-75.

Punam, P., Kumar R., Sharma S., and Atul, D. (2012). "The effect of organic management treatments on the productivity and quality of lemon grass (*Cymbopogon citratus)*," *Journal of Organic Systems* 7(5), 36-48.

Rafiee, E., and Shahebrahimi, S. (2012). "Nano silica with high surface area from rice husk as a support for 12-tungstophosphoric acid: An efficient nano-catalyst in some organic reactions," *Chinese Journal of Catalysis* 33(7-8), 1326-1333. DOI: 10.1186/2228-5326-2-29

Rafiee, E., Shahebrahimi, S., Feyzi, M., and Shaterzadeh, M. (2012). "Optimization of synthesis and characterization of nanosilica produced from rice husk (a common waste material)," *International Nano Letters* 2(29), 1-8. DOI: 10.1016/S1872-2067(11)60420-8

Rahman, M. M., Hasnida, N., and Wan Nik, W. B (2009). "Preparation of zeolite Y using local raw material rice husk as a silica source," *Journal of Scientific Research* 1(2), 285-291. DOI: 10.3329/jsr.v1i2.1777

Saceda, J. F., and De Leon, R. L. (2011). "Properties of silica from rice husk and rice husk ash and their utilization for zeolite Y synthesis," *Quimica Nova* 34(8), 1394-1397. DOI: 10.1590/S0100-40422011000800018

Samson, R., and Mehdi, B. (1998). "Strategies to reduce the ash content in perennial grasses," *Proceedings of Resource Efficient Agricultural Production-(REAP*), Ste. Anne de Bellevue, Québec, Canada, pp 3-8.

Srivastava, K., Shringi, N., Devra, V., and Rani, A. (2013). "Pure silica extraction from perlite: Its characterization and affecting factors," *International Journal of Innovative Research in Science, Engineering and Technology* 2(7), 2936-2942.

Terzioglu, P., Yucel, S., Rababah, T. M., and Özçimen, D. (2013). "Characterization of wheat hull and wheat hull ash as a potential source of SiO_2," *BioResources* 8(2), 4406-4420. DOI: 10.15376/biores.8.3.4406-4420

Umeda, J., and Katsuyoshi, K. (2008). "Process optimization to prepare high-purity amorphous silica from rice husks via citric acid leaching treatment," *Transactions of JWRI* 37(1), 13-17.

Umeda, J., Kondoh, K., and Mitchiura, Y. (2007). "Process parameters optimization in preparing high-purity amorphous silica originated from rice husk," *Materials Transaction* 48(12), 3095-3100.

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