Preparation and Characterization of Active SiO_2 from *Cymbopogon citratus* Ash Calcined at Different Temperature

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Cymbopogon citratus or lemon grass, is a potential renewable herbaceous biomass alternative. Lemon grass contains silica, which is available for extraction as a filler for various applications. Lemon grass ash is produced at calcination temperatures of 0, 400, 525, 600, and 700 ˚C. The silica content of the lemon grass ash was characterized by X-ray fluorescence (XRF), X-ray powder diffraction (XRD), scanning electron microcopy (SEM), and Fourier transform infrared (FTIR) analysis. The shape and texture of the lemon grass ash were studied by SEM. The highest silica content recorded was 24.00% for lemon grass calcined at 400 °C. The porosity of the lemon grass ash increased as the calcination temperature increased from 0 °C to 700 °C. XRD analysis showed that the crystallinity of silica in the lemon grass ash increased with increasing calcination temperature. FTIR analysis confirmed the presence of organic structure in lemon grass without calcination and the inorganic structure of siloxane and silanol bonds present in lemon grass calcined at different temperatures.

Keywords: Silica; Inorganic compounds; Mechanical treatment; Crystallinity

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INTRODUCTION

Cymbopogon citratus (lemon grass) is a tall, coarse grass with rhizomes and densely tufted fibrous roots (Adekomi *et al.* 2012). The plant is a native herb of India and is cultivated in other tropical and subtropical countries such as South Africa, Sri Lanka, Indonesia, Thailand, and Malaysia (Nambiar and Matela 2012). The most suitable temperature for lemon grass cultivation is between 18 °C to 29 °C at a soil pH of 5.0 to 5.8 (Punam *et al.* 2012). Lemon grass reportedly contains 1% to 2% of essential oil on a dry basis. The oil is usually extracted and used as a raw material in food, cosmetic, and pharmaceutical industries (Paviani *et al.* 2006).

Lemon grass also has many contributions in the medical field. This aromatic plant is used as a folk remedy for coughs, gingivitis, malaria, pneumonia, and vascular disorder (Oloyede 2009). Lemon grass consists of crude protein (15.68%), ash (23.40% to 25.00%), crude fiber (27.72%), fat (1.25%), and carbohydrates (38.44%) (Adegbegi *et al.* 2012). Besides, proximate analysis showed that this plant consists of many important minerals such as silica, phosphorus, potassium, and zinc. However, the amount of minerals that can be found in lemon grass can vary according to the methods of sample preparation and experimentation (Aftab *et al.* 2011). According to Ogie-odia *et al.*

(2010), the silica body is mostly present on the adaxial surface. This silica can be extracted and used as a source of amorphous or porous silica.

In general, commercial silica such as quartz and feldspar is present in most rock. The type of silica present can be different depending on what type of rock is being considered. Besides, silica which is abundant in soil and rock can also be transmitted to the tissue of root plants such as rice husk, wheat husk, sugar cane, and lemon grass (Pekarovic *et al.* 2006). Therefore, silica can be extracted from these plants to be used as an alternative source for the commercial silica that is presently being utilized in industry (Terzioglu *et al.* 2013). Silica is used widely in glass, ceramic, polymer composite, cement, pharmaceutical, cosmetic, and detergent industries (Kalapathy *et al.* 2002). Furthermore, silica is used as catalyst and as a thin film or coating for electronic and optical materials (Kalapathy *et al.* 2000; Okoronkwo *et al.* 2013).

According to Pekarovic *et al.* (2006), silica is soluble in highly alkaline solutions. Silica from natural fiber is usually extracted or precipitated from ash content by implementing the acid washing and gasification methods. These methods are popularly utilized for recovering silica from rice husk and bagasse (Okoronkwo *et al.* 2013; Samsudin *et al.* 2009). According to Javed *et al.* (2009), two types of silica are produced by the combustion process: amorphous (lechatelierite) and crystalline (crystobalite) forms. In general, amorphous silica is used as an absorbent and catalyst support in different chemical syntheses because of its high purity, small particle size, and high surface area. Amorphous silica is formed at calcination temperatures between 400 °C and 600 °C, while crystalline silica is formed above 700 °C. Therefore, the main objective of this study was to characterize silica content in lemon grass calcined at 400 °C to 700 °C by mechanical treatment. The silica obtained through this method will be used as filler in polymer composite.

EXPERIMENTAL

Materials

Lemon grass leaves were obtained from Stesen Agroteks UniMAP Perlis, Malaysia. This lemon grass was cultivated in a clay-heavy soil that contained a high silica content. The leaves were washed using tap water to remove impurities, dried at 105 °C for 24 h in a circulated oven, and then ground to pieces smaller than 1 mm in diameter using a grinder (model RT-34, Rong Tsong, Taiwan). Subsequently, the leaves were sieved to 20-mesh size using a sieving machine (model T-20, NL Scientific, Malaysia) to obtain the required sample size. The sample was again dried in the circulated oven according to the TAPPI Test Method for Determination of Total Solids in Biomass and Total Solids in Liquid Process Samples (T412 om-02). Then, the sample was treated in a muffle furnace (model L6-1200, Jinyu, China) under different temperatures at 400, 525, 600, and 700 °C according to the TAPPI Test Method for ash in wood, pulp, paper, and paperboard, with a combustion at 525 °C (T 211 om-07). While lemon grass without calcination was used as the control condition.

Silica Characterization

The sample was characterized by X-ray fluorescence (XRF), X-ray powder diffraction (XRD), scanning electron microcopy (SEM), and Fourier transform infrared (FTIR) analysis. Chemical composition of lemon grass was determined by X-ray fluorescence (XRF) with a PANanalytical MiniPAL 4 X-ray spectrometer (Philips, UK). The phase identification of extracted silica was determined using the Bruker D2 phaser X-ray diffractometer with Cu-Kα1 radiation of λ = 1.54Å, generator tension of 30 kV, and generator current of 10 mA in the 2θ range of 10° to 80° at 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 Gaussian functions for each peak (Saceda 2011). CI was calculated using Eq. (1):

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

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

The SEM analysis was carried out using computer-controlled field emission SEM (model JEOL JSM 6460 LA, JEOL, USA). Fourier transform infrared spectroscopy (FTIR) spectrum was recorded with a Perkin Elmer (model L1280044 Perkin Elmer, USA) instrument. The diffuse reflectance infrared Fourier transform technique was used for all samples to identify types of chemical bonds (functional groups). 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 1 shows the chemical composition of lemon grass without calcination and lemon grass calcined at various temperatures. Lemon grass without calcination recorded the lowest content of silica, which is 10.9%. However the silica content of lemon grass increased after calcination. According to Luduena *et al.* (2011), the calcination process will remove cellulose, hemicellulose, and lignin present in the cell wall of the materials, thus increasing the mineral content of the specimen. The highest silica content, 24.0% was recorded for lemon grass calcined at 400 °C. Besides, the silica content of lemon grass calcined at higher temperature from 525 to 700 °C was observed to decrease from 22.2 to 19.6%.

The other metallic elements present in the lemon grass without calcination and lemon grass calcined at various temperatures are shown in Table 1.

Table 1. Chemical Composition of Lemon Grass without Calcination and Lemon Grass Calcined at Various Temperatures

Components	Lemon Grass without calcination (%)	Lemon Grass calcined at 400 °C (%)	Lemon Grass calcined at 525 °C (%)	Lemon Grass calcined at 600 °C (%)	Lemon Grass calcined at 700 °C (%)
SiO_2	10.9	24.00	22.2	21.6	19.6
MgO	2.0	2.3	2.6	2.7	3.1
K_2O	47.27	39.04	37.11	36.98	36.58
CaO	25.3	20.0	20.1	21.8	23.7
Fe_2O_3	0.29	0.215	0.257	0.258	0.32
P_2O_5	3.91	6.04	7.09	7.75	8.12

Table 1 shows that the concentration of K_2O decreased as the calcination temperature of lemon grass increased. Other organic elements such as MgO, CaO, and P_2O_5 increased as the calcination temperature increased. This is due to the decomposition of larger and complex molecules into smaller molecules such as oxide group, CO_2 and H_2O (Wong *et al.* 2014). Besides, alkaline metal such as potassium is soluble in water. Therefore, the molecules are washed out by the distilled water that was used during washing process (Allcock 2008).

X-ray Powder Diffraction (XRD)

X-ray diffractograms of lemon grass calcined at various temperatures are presented in Fig. 1. The results show that lemon grass calcined at 0 °C contained only amorphous silica. This was apparent because of the single hump peak centered at 21.8° hkl (203) (Kalapathy *et al.* 2000). According to Okoronkwo *et al.* (2013), the diffraction broad peak = 22° indicates the presence of amorphous silica and the low amount of crystalline silica. After calcination at various temperatures, the ash obtained its white-grey color, whereas raw lemon grass is green in color. The XRD patterns of lemon grass ash calcined between 400 °C to 700 °C had many sharp peaks that indicated crystallinity (Abdul-Basit and Ra'id 2013). As shown in Fig. 1, lemon grass calcined at 700 °C exhibited the highest amount of crystalline silica because of the presence of the highest sharp peak at 28.80° hkl (135) [PDF 01-073-7801]. The succeeding high XRD peaks and intensity in decreasing order were 600, 525, and 400 °C, with values of 28.62° hkl (261)[PDF 01-089-7499], 28.53° hkl (135) [PDF 01-089-7499], and 28.32°hkl (310)[PDF 01-073-7801], respectively (Chirayil *et al.* 2014). Moreover, the total crystalline silica content in lemon grass ash increased as the calcination temperature increased from 400 °C to 700 °C, as indicated in Table 2. The results show that lemon grass calcined at 700 °C had the highest crystallinity degree, which was 62.90% as compared to that of the other lemon grass ash. According to Siti Haslina *et al.* (2012), crystallization growth depends on crystallization temperature. The increase in calcination temperature contributed to the increased energy supply for the nucleus to achieve the activation energy for crystal growth, which increased the degree of crystallization.

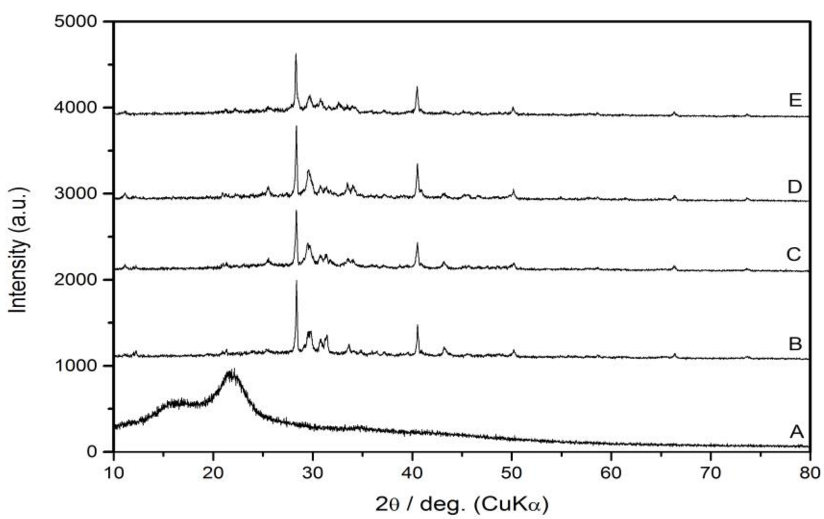

Fig. 1. X-ray diffraction pattern of lemon grass calcined at temperatures: (A) without calcination (B) 400 °C, (C) 525 °C, (D) 600 °C, and (E) 700 °C

Table 2. Crystallinity Index of Lemon Grass Calcinated at Various Temperatures

Lemon grass calcination temperatures (°C)	Crystalline structure (%)	Amorphous structure (%)
Without calcination	36.20	63.80
400	49.30	50.70
525	53.90	46.10
600	55.00	45.00
700	62.90	39.50

Scanning Electron Microcopy (SEM)

A morphological study of lemon grass before and after calcination at different temperatures is presented in Figs. 2 to 6. Figure 2 shows the fibrillation of lignocellulosic material, which is attributed to the mechanical treatment of the lemon grass before calcination. Fibrillation occurs in the cell wall structure of lemon grass which undergo the mechanical treatment process. This process will partially delaminate the cell wall structure of the lemon grass.

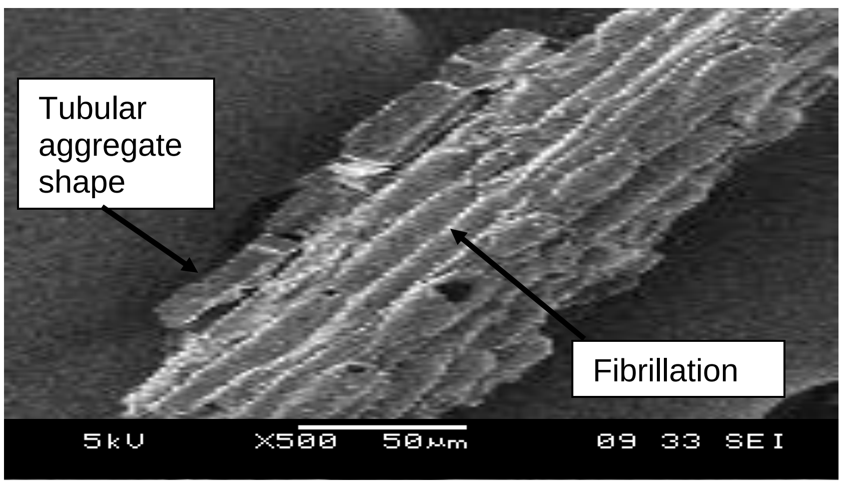

Fig. 2. SEM images of lemon grass without calcination

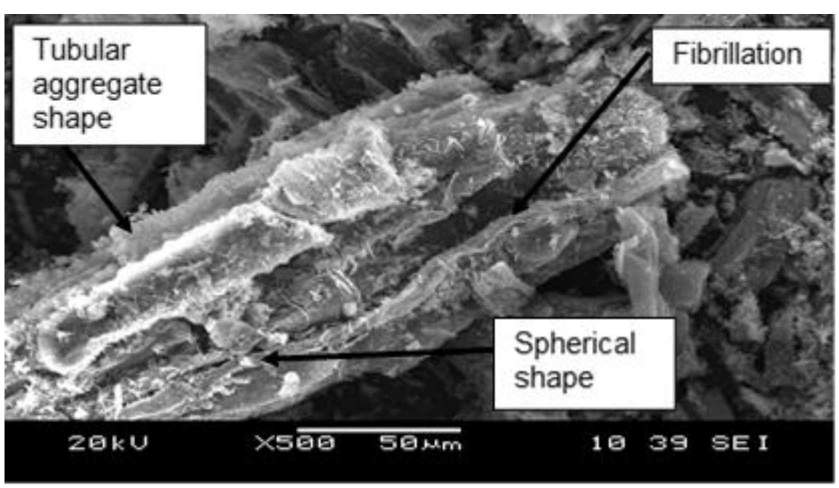

Fig. 3. SEM images of lemon grass calcined at 400 °C temperature

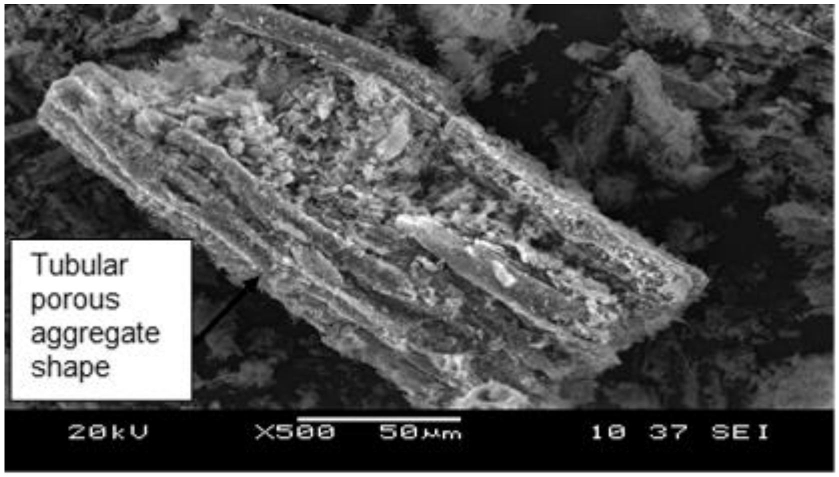

Fig. 4. SEM images of lemon grass calcined at 525 °C temperature

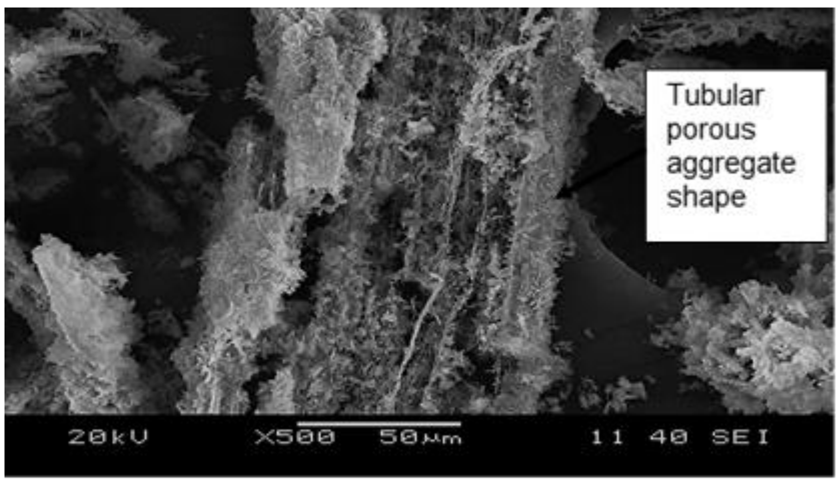

Fig. 5. SEM images of lemon grass calcined at 600 °C temperature

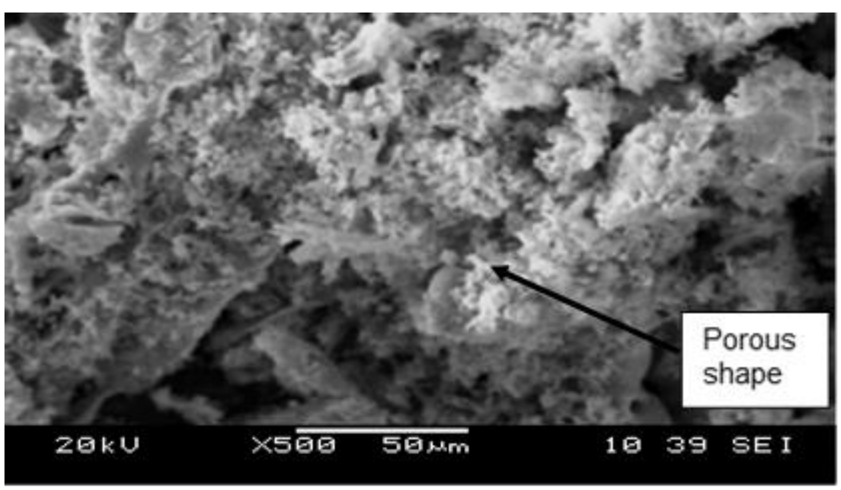

Fig. 6. SEM images of lemon grass calcined at 700 °C temperature

The morphology of the lemon grass after calcination at 400 to 700 °C changed from a tubular aggregate shape to tubular porous aggregate and porous shaped as compared to lemon grass without calcination. These characteristics are due to the removal of the hemicellulose, cellulose, and lignin after calcination at various temperatures (Borlini *et al.* 2008). Moreover, the presence of tubular aggregate indicates that lemon grass ash contains minerals such as silica (Si), potassium (K), and calcium (Ca), whereas porous aggregates indicate the lemon grass content of alkaline earth metals such as calcium (Ca) and magnesium (Mg) (Ul-Haq and Malik 2014). Alkaline earth metals exhibits low density materials which impart the porous element in lemon grass ash (Allcock 2008). In addition, spherical shapes are also present in Figs. 3 to 6 due to the existence of crystalline silica in the lemon grass after calcination.

Fourier Transform Infrared (FTIR) Analysis

FTIR spectroscopy was conducted to study the presence of functional groups in lemon grass before and after calcination. As can be observed in Fig. 3, the spectrum of lemon grass without calcination (A) contained prominent absorption bands at 3315, 2918, 1732, 1616, 1372, 1243, 1034, and 862.30 cm^{-1} which correspond to the stretching vibrations of H-OH, C-H symmetrical stretching, C=O stretching of hemicellulose and aromatic ring vibration of lignin. Peaks recorded at 1372 cm^{-1} and 1243 cm^{-1} correspond to the C-H bending of cellulose. Moreover, the inorganic parts related to Si-O-Si bond was recorded at peaks 1034 and 862.30 cm^{-1} (Luduena *et al.* 2011). Lemon grass without calcination exhibited the highest band for water adsorption (3315 cm^{-1}) because of the hygroscopicity of lemon grass fiber (Khemthong *et al.* 2007). Lemon grass fiber is hydrophilic in nature; therefore, the hydroxyl group present in the cell wall structure of the lemon grass forms the hydrogen bonds with water molecules (Music *et al.* 2011).

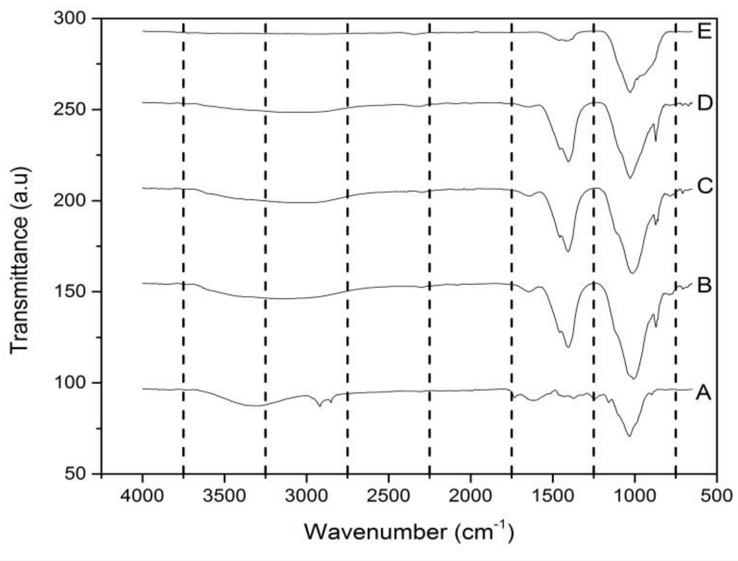

Fig. 3. The FTIR spectra of lemon grass calcined at temperatures (A) without calcination, (B) 400 °C, (C) 525 °C, (D) 600 °C, and (E) 700 °C

However, lemon grass after calcination contained only the inorganic parts with the elimination of organic parts such as cellulose and hemicellulose. Referring to Table 3, strong peaks were observed on lemon grass calcined at 400 to 700 °C, which were between 1430 cm^{-1} to 1350 cm^{-1} with the addition of shoulder peaks between 1644 cm^{-1}.

The strong absorption was assigned as the TO component of the asymmetric vibrations of O-Si-O bridges. The shoulder peak was assigned to the LO components of the same vibration. This downshift in the peak frequency was attributed to the presence of high amounts of sodium (Na), calcium (Ca), magnesium (Mg), and phosphorous (P) ions in lemon grass after calcination (Karakassides *et al.* 1997). Moreover, the strongest broad IR band was recorded between 1034 cm^{-1} to 1029 cm^{-1}. This range is usually assigned to the TO component of the asymmetric vibrations of O-Si-O bridges. Moreover, the additional band appeared at calcination temperatures between 400 °C to 600 °C. This additional band is attributed to the siloxane ring in the silica network, which appeared in the lemon grass ash as the calcination temperature increased to 600 °C (Wan Ab Karian Ghani *et al.* 2008).

Table 3. Infrared Spectra of Lemon Grass Calcined at Various Temperatures

Wavenumber (cm^{-1})					
Vibrational band assignment	Lemon grass without calcination	Lemon grass calcinated at 400°C	Lemon grass calcinated at 525°C	Lemon grass calcinated at 600°C	Lemon grass calcinated at 700°C
Si-OH or H-OH stretch	3315.38 1372.69 -	3142.75 1405.97 1644.65	3060.27 1408.11 1644.00	3055.60 1405.43 -	- 1428.50 -
Aromatic ring vibration	1616.85	-	-	-	-
C-H symmetrical stretch	2918.84	-	-	-	-
Carboxylic acid C=O group stretch	1732.69	-	-	-	-
C-H bending	1243.44	-	-	-	-
Si-O-Si asymmetric stretch	1034.30	1013.22	1012.27	1027.45	1029.27
Si-O-Si symmetric stretching	862.30 -	871.42 707.53	873.08 708.33	872.56 709.22	- -

CONCLUSIONS

1. Lemon grass ash was obtained by calcination at various temperatures. The highest value of silica content of 24.00% was recorded at 400 °C calcination temperature.

2. The crystallinity of silica in lemon grass ash increased from 36.2% to 62.9% as the calcination temperature was increased from 400 °C to 700 °C.

3. The FTIR analysis showed the presence of siloxane (Si-O-Si) and silanol (Si-OH) groups in the lemon grass ash as the calcination temperature increased from 400 °C to 700 °C.

4. SEM analysis showed the presence of tubular porous aggregates of spherical and porous particles in lemon grass ash as the calcination temperature increased from 400 °C to 700 °C.

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