Silica nano particles synthesized from boiler spent ash: Value addition to an industrial waste

Rani Abraham[1] (Corresponding author), Sanal S[1], Jacob Thomas[3], Jacob George[2], Desy P. Koruthu[1], Manivarnan N.K.[1]

[1]Department of Chemistry, Christian College, Chengannur, Kerala, India-689122

Tel: +919447439962 E-mail: raniabraham@gmail.com

[2]Department of Physics, Christian College, Chengannur, Kerala, India-689122

[3]Eastern Condiments (Pvt) Ltd., Eastern Towers, Edapally, Kochi, India

Abstract

Large quantities of biomass ash are generated everyday by the spice industries and are currently disposed off as landfill. However, this could transform into an environmental pollutant unless alternative techniques are developed for its disposal or value addition. Here in this study, the waste ash from biomass combustion wassuccessfully converted into silica nanoparticles with potential for application in several fields. The highly alkaline nature of the ash and presence of unburned carbon warrants a pretreatment which includes digestion and acid treatment. The synthesized silica was characterized in terms of morphology, specific surface area, crystallinity, surface functional groups and size. Alkaline extraction of the pretreated ash followed by acid precipitation yielded an amorphous structure with minimum mineral contaminants, high surface area, and a narrow size distribution (8-10 nm range) characteristic of nano silica. Studies thus indicate that the waste ash and the extraction process could be fine tuned for the large scale production of amorphous silica and could be of use to solve the problem of boiler ash pollution.

Keywords: biomass ash, boiler ash, nano silica, value addition to waste, amorphous silica

1. Introduction

 Spent biomass obtained after extraction of color and oleoresin from spices like chilli, turmeric, pepper, coriander, ginger etc. is used as boiler fuel in the spice industries. Boiler ash which is a solid waste has become a matter of concern due to the very large volumes produced daily and difficulty in disposal. India being a major player in global spice trade the number of such industries is expected to increase in future owing to greater interest in natural colours and flavours. The ash contain about 10-20% silica [1] along with potassium, calcium and magnesium salts and their oxides, which are the major components. Due to the alkaline nature of the ash the silica contained in it could be easily solubilized and extracted. Though there are several studies on the extraction of fine silica from various sources like rice hull, rice husk ash, bagasse ash [2,3] oil shale ash [4,5], in most cases the presence of crystalline phases like cristobalite and trydimite and silanol groups in the ash renders the silica less active [6].

Silica (SiO_2) in nano dimensiona also known as silica nanoparticles or nanosilica are materials with a wide array of interesting applications. They make excellent heterogeneous catalysts and catalyst supports due to their high surface area and porous nature [7], as reinforcing agents in concrete [8], as additives for rubber and plastics [9,10] in paints [11] in coatings [12,13] and as promising materials for experimental dental nanocomposites [14]. Silica nano particles are also the basis for a great deal of biomedical research due to their stability, low toxicity and ability to be functionalized with a range of molecules and polymers. These could be used as a stable non toxic platform for biomedical applications such as drug delivery [15]. Though nanoscale silica materials are at present prepared using methods which include vapour phase reaction, sol-gel and thermal decomposition techniques [16] their wide spread use is limited by high cost and energy. It is in this context that methods of preparation of silica from biomass ash need to be considered as viable alternative green methods due to the relatively low cost, low energy consumption and ease of extraction.

In continuation of our studies [1] on the value addition of this waste material we investigated the potentiality of using biomass ash from the oleoresin industry as a source for amorphous nano silica. The synthesized silica particles were studied by X-ray diffraction, surface area measurements, SEM, EDAX, TEM and FTIR techniques.

2. Experimental

2.1 Materials and methods

The ash used in this study was obtained from Akay Flavours and Aromatics, an oleoresin industry in Kochi, India. The ash was refluxed with water (1:1 ratio) for the removal of water soluble salts, filtered and dried. The dried ash was then suspended in water (1: 9 ratio), pH adjusted to be in the acidic range (pH=5) by addition of

6N/1N HCl or H2SO4and refluxed. The treated ash was filtered, washed and dried overnight in an air oven and later activated at 600°C for one hour in a muffle furnace.

2.1.1. Preparation of silica from the pretreated ash

100 g of the pretreated ash was refluxed in 2N NaOH (300 ml) for 2-3 hours and filtered while hot. Silica is precipitated from this sodium silicate solution using sulphuric acid. For this, the filtrate is heated to 80-900C and stirred continuously while adding 6N H2SO4 slowly dropwise (otherwise chemistry of reacting mass may change along with physical properties) until acidic conditions indicate approximately complete precipitation of silica from sodium silicate. This silica is separated from the colloidal solution by repeated centrifugation and washing till the centrifugate tests negative for sulphate ions (using 0.1N BaCl2 solution). The silica was dried in an air oven and later activated at 600 C for one hour. Silica obtained from ash pretreated with hydrochloric acid and sulphuric acid are hereinafter referred to as silica A and silica B respectively.

2.2 Characterization of the synthesized silica particles

Powder X-ray diffraction measurements were done on a diffractometer model Bruker AXS D8 Advance using Ni K filter and Cu Kα (λ= 1.5406 Å) radiation at room temperature. Nitrogen adsorption analyses were carried out in a Micromeritics TriStar 3000 V6.07A instrument. Experiments were performed isothermally at -195.800°C. Samples (ca 80 mg) were previously degassed under vacuum at 300°C for 4-5 hours. Data were processed by the BET equation. Scanning electron microscopy was carried out on a Jeol JSM-6390 LV instrument with an accelerating voltage of 20kV and elemental was carried out on a Jeol Model JED-2300 EDS system coupled with the scanning electron microscope. Samples were mounted on double sided carbon tape on the SEM stub. Several fields of view were selected and carefully analyzed and the surface composition within selected area was analysed by EDX. Fourier Transform infrared spectroscopic measurements were done using a Thermo Nicolet Avatar 370 model with a resolution of 4cm^{-1} in the spectral range 4000-400 cm^{-1} using KBr disc method. . Further confirmation of morphology and particle size was done by transmission electron microscopy using a Philips make transmission electron microscope CM 200 model.

3. Results and Discussion

A pretreatment of the ash was done to remove the metallic compounds present in the ash to the maximum extent possible. This pretreatment step is necessary as metallic impurities are reported to substantially influence the quality of silica from the ash [17]. The ash has a high content of potassium which melts on the surface and accelerates the crystallization of amorphous silica and carbon fixation in the ash. Interaction between the metallic ions and silica could also lead to a considerable decrease in surface area. Hydrochloric acid and sulphuric acid were used for pretreatment of the ash as they could react with metallic impurities effectively and these dissolved compounds leached out of the solution during filtration. The pretreated ash was digested and the digested ash had a lighter colour compared to the undigested ash. Burning of carbon in the ash or removal of other volatile impurities could be the reason for this change of colour.

X-ray powder diffraction is the most used technique for identification of crystalline phases in a sample. X-ray diffractograms of silica obtained from HCl pretreated ash (silica A) exhibits a broad peak ranging from a 2θ value of 15° to 33° (Figure 1). This broad peak or hump as it is usually referred to, is a characteristic of amorphous silica. The amorphous nature of silica also implies a high pozzolanic activity [18] because of much higher solubility in water compared to crystalline forms like quartz and higher surface area. That no other peaks are seen in the diffractogram confirms the absence of any ordered crystalline structure in the material. The XRD pattern of silica obtained from sulphuric acid pretreated ash (hereinafter referred to as B) on the other hand contains several peaks corresponding to different mineral impurities present. The effect of HCl and H2SO4 pretreatment in removing the metallic impurities is thus evident. Sulfuric acid pretreatment is not adequate in removing the metallic oxides while HCl does the job more efficiently. For the silica A the maximum of the broad peak is at 23.56 radians; this relates to an average Bragg distance of d = 0.3773 nm. (For ground quartz powder 2θ = 26.5° and d = 0.336 nm). This

enlargement of the average atom distance reveals markedly disordered atom arrangement of the SiO4 units in silica [19].

The reactivity of silica as a catalyst or as a concrete additive depends on its surface area and porous nature and hence surface area is an important parameter of the material. BET method was adopted for the surface area analysis of the samples which gave a value of 432 m^2/g for surface area of A and a value of 15m^2/g for

surface area of B. Such a high surface area corresponds to decreased particle size for silica A while the low surface area of sample B corresponds to the presence of mineral species which could not be washed off by sulphuric acid pretreatment. The particle size could be calculated from the specific surface area [18] by taking into consideration the well known relationship SA × ds × ρ = 6×103, where SA is the surface area, d_s

= average particle diameter and ρ, the density of silica. Taking the density of silica as 2.2 gram/cm^3, which is the density of amorphous, anhydrous nonporous silica, a value of 6.3 nm is obtained for d_s.

Scanning electron micrographs show a difference in the surface morphology of the two samples. Micrographs at different optical magnifications were analysed. Differences in the tendency of particles to clump together could be seen at lower magnifications (figures 2a & 2b), while variations in size and morphology become clear at higher magnifications (figures 3a & 3b). Surface morphology indicative of a high surface area which seems adequate for specific applications such as special ceramics material, catalyst support or construction material could be traced from scanning electron microscopic studies of sample A. SEM of silica B on the other hand shows a non porous surface morphology. An EDX analysis (Fig.4) of silica A shows the presence of traces of Al which could be present as an oxide along with silica. This aluminium oxide naturally present in the silica could be also acting as a stabilizer for the silica. Excess oxygen percentage is attributed to the associated water molecules or "free" water (moisture) present. EDX analysis of silica B shows a higher percentage of C, Na and S. Repeated washing of the precipitated failed to remove these surface adsorbed species. Presence of mineral species even after pretreatment of the ash could have accelerated the fixation of carbon and other species on the surface making its removal difficult.

Further substantiation of size and morphology of silica A was obtained from transmission electroscopic studies. TEM images (Fig. 5) show the size and morphology of the synthesized particles. The particles seem to be mono disperse in the narrow range of 8-10 nm, a diameter slightly higher than that calculated from specific surface area. In general, the particle diameter calculated from specific surface area will be smaller than the diameter that would be judged by eye from transmission electron micrographs, because smaller particles may remain unobserved yet contribute substantially to the specific surface [18]. The morphology observed is as expected for amorphous silica particles as the sol particles often have a tendency to adopt the spherical shape so as to reach a minimum of interfacial surface area.

The FTIR spectrum shown in figure 6 agrees well with the spectrum for standard silica. Increase in line width is due the amorphous nature of the material. Amorphous silica has broad peaks compared to the narrow lines observed for crystalline silica. The strong absorption bands at 1087 cm^{-1} and 463 cm^{-1} originate from the asymmetric stretching of Si-O and flexural vibrations of Si-O-Si bonds while that at 800 cm^{-1} could be attributed to the vibrations of (SiO4) tetrahedrons [20]. The peaks at 3447 cm^{-1} and 1642 cm^{-1} corresponds to water molecules adsorbed on the hydrophilic surface silanol groups of the silica bands [17]. It is the silanol groups that contribute to the pozzolanic activity. Use of colloidal silica nano particles with pozzolanic activity, high surface area and fine particle size in concrete mixtures is said to increase the strength of concrete remarkably

4. Conclusions

Extraction of amorphous silica nano particles from the biomass spent ash of the oleoresin industries were successfully done after pretreatment of the ash with hydrochloric acid. The particles have an excellent surface area as indicated by BET method and a porous surface from SEM images. XRD studies indicated amorphous nature of the material while the transmission electron microscopic image exhibited mono dispersed particles with ~10 nm size. The amorphous nature of the silica, high surface area and fine particle size combined with its low production cost makes it an ideal candidate for use in high performance concrete and other applications in construction. High surface area silica nano particles also find use as a support in catalysis. This study thus provides a route to value addition or utilization of the spice industry waste.

Acknowledgement

References

[1] Abraham , R., George, J., Thomas, J. & Yusuff, K. K. M. (2013). Physicochemical characterization and possible applications of the waste biomass ash from oleoresin industries of India. *Fuel*, 109, 366-372.

[2] Liou, T- H. (2004). Preparation and characterization of nano-structured silica from rice husk. *Mater Sci Engg A,* 364, 313-324.

[3] Thuadaij, N., Nuntiya A., & Mai, C. (2008). Preparation of Nanosilica Powder from Rice Husk Ash by Precipitation Method. *J. Sci* , 35(1), 206-211.

[4] Gao, G-.M, Miao, Li-Na,. Ji,, G-J, Hai-Feng, Z. & Shu-Cai, G. (2009). Preparation and characterization of silica aerogels from oil shale ash. *Mat Lett*, 63, 2721–2724.

[5] Gui-Mei, G., Hai-Feng, Z., Shu-Cai, G., Zhao-Jun, L., Bai-Chao, A., Ji-Jin, X. & Guang-Huan L (2009) Preparation and properties of silica nanoparticles from oil shale ash. *Powder Technol,* 191, 47–51.

[6] Petkowicz, D. I, Rigo R. T., Radtke, C., Peigher, S. B &, dos Santos & J. H. Z. (2008). Zeolite NaA from Brazilian chrysotile and rice husk. *Micropor Mesopor Mater*., 116(1-3), 548-554.

[7] Polshettiwar, V., Cha, D., Zhang, X. & Basset, J. M. (2010). High surface area silica nanospheres (KCC-1)

with fibrous morphology. *Angew Chem. Int Ed*., 49, 9652-9656.

[8] Dunster, A. (2009). Silica fume in concrete. Information paper N° IP 5/09, IHS BRE Press, Garston, U.K.

[9] Chen, Y., Peng, Z., Kong, L. X., Huang, M. F. & Li, P. W. (2008). Natural rubber nanocomposite reinforced with nano silica. *Polym Eng Sci.,* 48(9), 1674-1677.

[10] Pradittham, A, Trejitwattanaku, S., Sramanee, T., Thanakkasaranee, S., Atong, D. & Pechyen, C. (2012). Preparation of LLDPE/modified silica nanoparticle with triethoxysilane film for microwaveable packaging. *Adv Mat. Res*., 488-489,1525-1529.

[11] Mochizuki, D., Tamura, S., Yasutake, H., Kataoka, T., Mitsuo K., & Wada, Y. (2013). A photostable bi-luminophore pressure-sensitive paint measurement system developed with mesoporous silica nanoparticles. *J Nanosci Nanotechnol* 13(4), 2777-81

[12] Ogihara, H., Xie, J., Okagaki, J., Saji, T. (2012). Simple method for preparing superhydrophobic paper: spray – deposited hydrophobic silica nanoparticle coatings exhibit high water-repellency and transparency. *Langmuir,* 28(10, 4605-4608.

[13] Palanivel, V., Zhu, D., van Ooij, W. J. (2003). Nanoparticle-filled silane films as chromate replacements for aluminum alloys. *Prog Org Coatings*, 47(3-4), 384-392.

[14] Rahim, T. N. A. T., Mohamed, D., Ismail, A. R. & Akil, H. M. (2011). Synthesis of nanosilica fillers for experimental dental nanocomposites and their characterizations. *J Phys Sci* , 22(1), 93-105.

[15] Chen, Y., Xu, P., Chen, H., Li, Y., Bu, W., Shu, Z.., Li,Y., Zhang, J., Pan, L., Cui, X., Hu, Z., Wang, J., Zhang, L. & Shi, J.. (2013). Colloidal HPMO Nanoparticles: Silica-Etching Chemistry Tailoring, Topological Transformation and Nano-Biomedical Applications. *Adv. Mater*., 25, 3100.

[16] Klabunde, K. J. (2001), *Nanoscale Materials in Chemistry*. Wiley-InterScience, New York, NY, USA,.

[17] Kamath, S. R. & Proctor, A.. (1998). Silica gel from rice hull ash: Preparation and characterization. *Cereal Chem.,* 75, 484.

[18] Iler, R. K., (1973) *Colloidal silica*, Edited by E. Matijevic, [in] Surface and Colloid Science, Vol. 6 Wiley, New York, p. 3.

[19] Kirk-Othmer, *Silica*. Edited by J.I. Kroschwitz and M. Howe-Grant,   Kirk-Othmer Encyclopedia of Chemical Technology, 4th edn Vol. 21, 1997, p. 977.

[20] Nakamoto, K. (2006), Infrared and Raman spectra of Inorganic and Coordination Compounds. Handbook of Vibrational spectroscopy, John Wiley & Sons Ltd,.
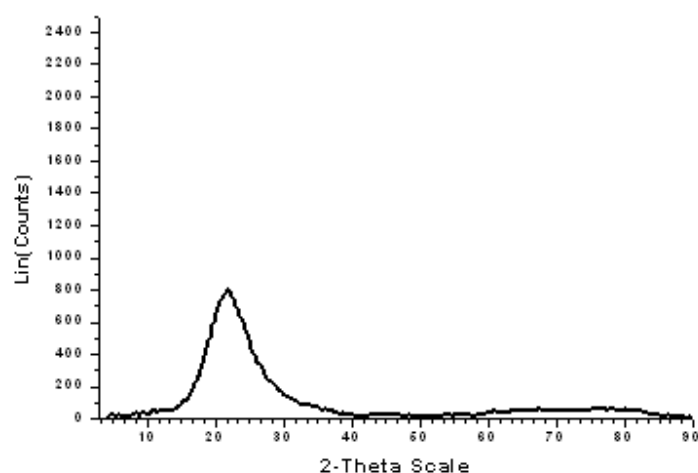
Figure 1. X-ray diffraction pattern of the silica synthesized from waste boiler ash showing a broad hump characteristic of amorphous silica
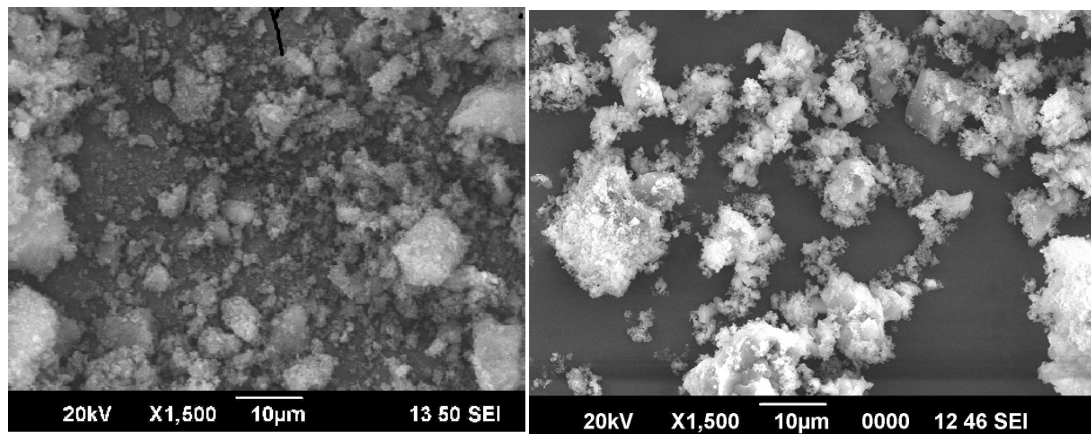
Figure 2 SEM images of the silica derived from (a) HCl pretreated ash and (b) H$_2$SO$_4$ pretreated ash at low magnification
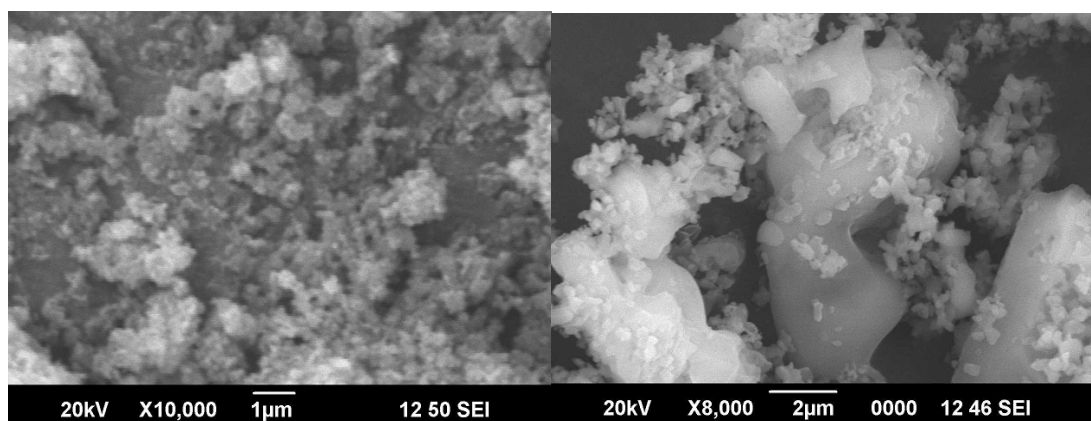

Figure 3. SEM images of the silica derived from (a) HCl pretreated ash and (b) H$_2$SO$_4$ pretreated ash at higher magnification
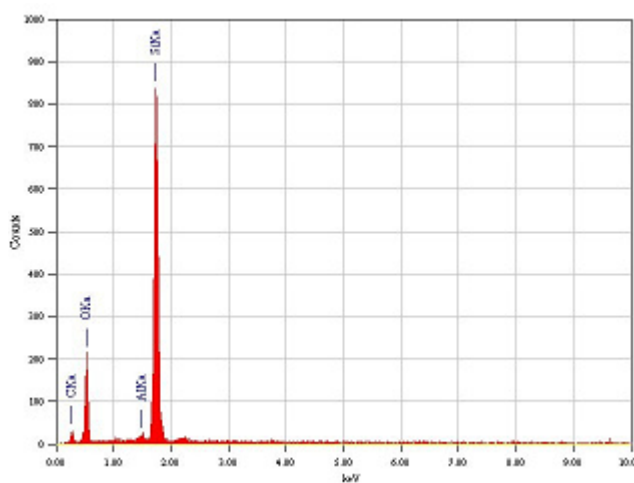

Figure 4. EDX of silica nano particles synthesized from waste boiler ash showing the surface and near surface composition
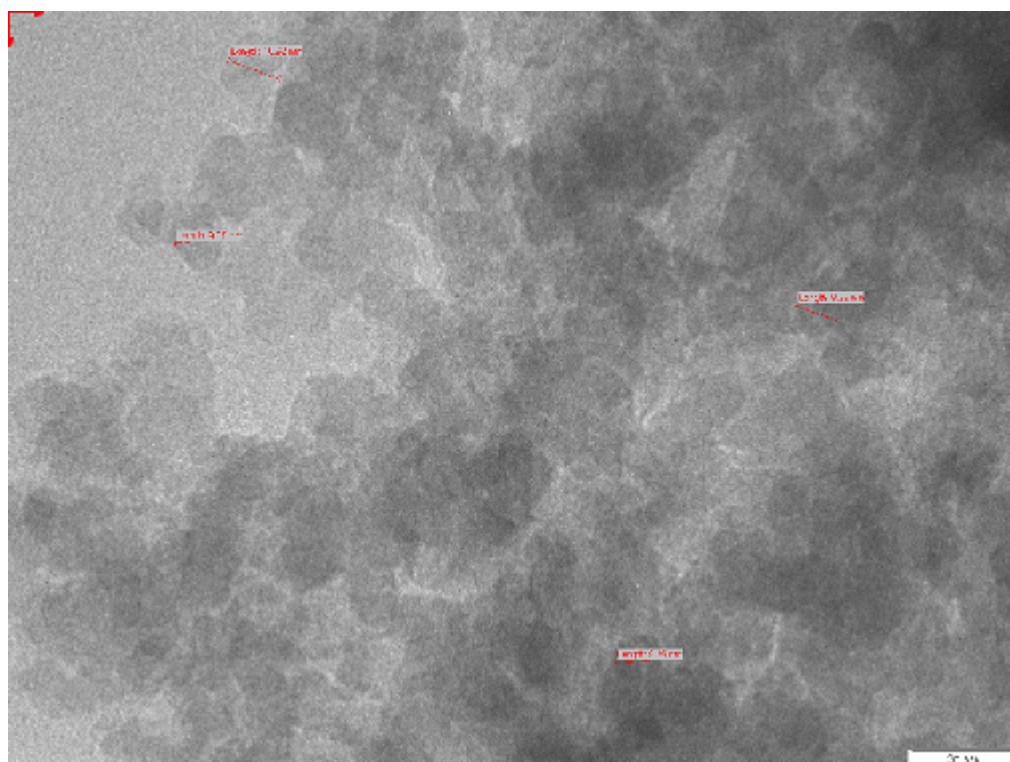
Figure 5. TEM image of silica synthesized from waste boiler ash showing nano sized particles
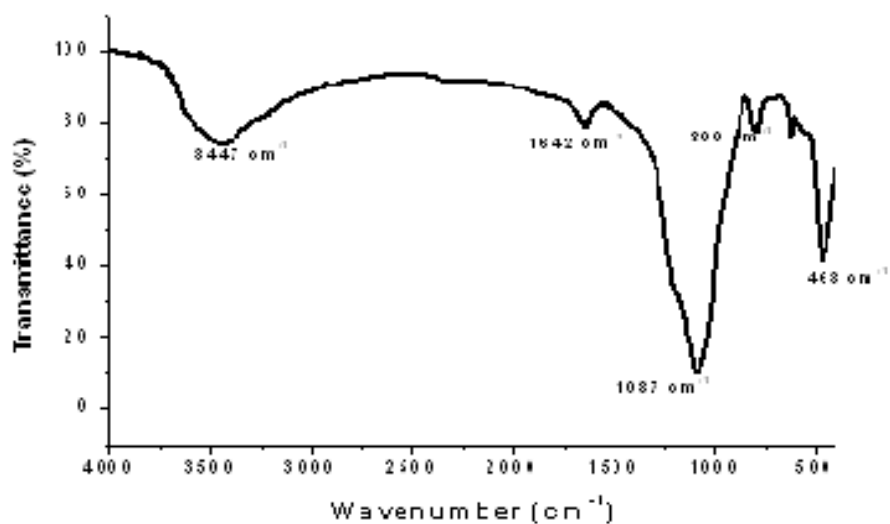

Figure 6 FTIR spectra of the silica synthesized from waste boiler ash exhibiting bands characteristic of silica

The IISTE is a pioneer in the Open-Access hosting service and academic event management. The aim of the firm is Accelerating Global Knowledge Sharing.

More information about the firm can be found on the homepage:
http://www.iiste.org

CALL FOR JOURNAL PAPERS

There are more than 30 peer-reviewed academic journals hosted under the hosting platform.

Prospective authors of journals can find the submission instruction on the following page: http://www.iiste.org/journals/ All the journals articles are available online to the readers all over the world without financial, legal, or technical barriers other than those inseparable from gaining access to the internet itself. Paper version of the journals is also available upon request of readers and authors.

MORE RESOURCES

Book publication information: http://www.iiste.org/book/

IISTE Knowledge Sharing Partners

EBSCO, Index Copernicus, Ulrich's Periodicals Directory, JournalTOCS, PKP Open Archives Harvester, Bielefeld Academic Search Engine, Elektronische Zeitschriftenbibliothek EZB, Open J-Gate, OCLC WorldCat, Universe Digtial Library , NewJour, Google Scholar