

## Preparation and Characterization of Nano Silica from *Equisetum arvense*

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### Abstract

With the progress of nanotechnology and increase in demand, several silica processing industries have started producing silica nanoparticles. As a result, the search for new sources capable of producing this material has been attracting the interest of many researchers. With this background, a study was carried out to obtain silica nano particles from the *Equisetum arvense*, a plant that possesses one of the highest amounts of silicon. This paper presents the preparation of nano silica particles with different combinations of acid washing and calcination at varying temperatures between 773 K and 873 K. The nanoparticles produced were characterized for nitrogen adsorption, morphology using transmission electron microscope and structural analysis by X-ray fluorescence and diffraction. It was found that nanoparticles produced by two cycles of acid washing and calcination at 773 K gave the best results, producing a material with white color, the highest specific surface area of about 330 m<sup>2</sup>/g with diameter of about 8 nm, and 93.5% of amorphous silica. The nanoparticles obtained can be potential industrial raw material for many applications.

**Keywords:** *Equisetum arvense*; Silica nanoparticles; Acid washing; Calcination; Surface area; Morphology

### Introduction

Nano-manufactured goods and nanotechnology, representing areas of scientific research and industrial applications, have been generating a lot of attention nowadays. As such, they have led to great expectations not only in the academic community, but also among investors, governments, and industrial sectors [1,2]. This is due to the unique characteristics possessed by nano structures, the properties exhibited by nano materials and the capability of the technology to fabricate new structures at atomic scale. All these result in the production of novel materials and devices that have great application potential. In fact, these materials have already become an industrial and economic reality. It is estimated that worldwide, the annual sources of naturally occurring nano particles is about 16.8 million tons from mineral aerosol, 3.6 million tons from marine salts and 1.8 million tons from biomass [3]. Of these, France alone produces annually about 485,000 tons of silica through approximately 1300 operators. This is due to nanoparticles having applications in a vast variety of fields with the sole purpose of manufacturing or to modify materials for a variety of technological uses [4].

Silica, as the main constituent of more than 95% of all the earth's rocks [5] and belonging to silicate compounds, is the common name for materials composed of silicon oxide (SiO<sub>2</sub>). It occurs both in crystalline and amorphous forms. However, despite the crystalline form being more abundant in the earth's crust, it has limited direct applications due to its low reactivity [6]. On the other hand, a pure form of silica with minimum impurities and amorphous nature is essential for the preparation of inorganic materials [7]. Hence, silica in amorphous nature has many industrial applications such as abrasives, advanced materials (SiC, Si<sub>3</sub>N<sub>4</sub>), cements, ceramic pigments, glasses, refractory, microelectronics, mortars, and zeolites [6-14]. Amongst many nano particles being produced, Silica Nanoparticles (SNP) has been receiving greater attention in the light of their possible uses in several scientific areas and in industrial segments [15-34] ([www.tsi.com/uploadedFiles/Site.../Nano-A4\\_5001286A\\_WEB.pdf](http://www.tsi.com/uploadedFiles/Site.../Nano-A4_5001286A_WEB.pdf)). These areas include agriculture, catalysis, energy, environment, human health and defense in the form of absorbents, thermal insulators and catalysts, as additives for cosmetics, medicines, printer toners, varnishes, foods and pesticides [6,11]. Besides, Nano silica also has biomedical and

biotechnological applications - for the controlled release of medicines and biosensors [9-11,13,15-27], particularly in cancer therapy and for the transfection of DNA. Accordingly, they have been produced on industrial scale [28-30].

In view of the above, nano silica is being produced from various sources, mostly from silica precursors such as silicon alkoxides, using several methods such as chemical processes involving vapor phase reactions, sol-gel and other techniques [31-35]. These processes are energy intensive due to the use of high temperatures, pressures, etc., and are not environmentally friendly or sustainable. Consequently, the search for new sources at cheaper costs and capable of producing amorphous nano silica of high quality by suitable environmentally friendly processes has been growing. It is reported that despite silica not being necessary for the healthy growth of any plant, it certainly seems to have some secondary effects such as 'playing a structural role or acting as a mineral barrier to both the invasion of pathogens and the translocation of bio-mineralized silica' [16]. Considering the biomass (lignocellulosic materials) has the capability of accumulating high amounts of silicon, and that hierarchical porous structures such as nano silica can be obtained from such structural hierarchy of plants [23,36-40], there are also a number of reports available in literature on the production of nano particles of silica (this is referred to as 'biogenetic silica') starting from biomass. The reason for this is due to its renewability and abundant occurrence, great potential for sustainability, low cost and the possibility to develop new materials. Therefore, the literature presents different methods, chemical and thermal, for the production of both pure and amorphous biogenetic

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silica. The biomass sources used for this purpose, including in the production of nano particles of cellulose, are plants (stem / barks/ fibers of banana, kenaf, pineapple leaf, sisal, *Phormium tenax* (harakeke), mengakuang leaf, mulberry bark), agro-industrial residues such as rice husk [5,35-48], sugarcane pulp, and coffee husk [48]. In all these cases, either alkali treatment coupled with high-pressure defibrillation and/ or acid treatment or steam explosion have been used. In fact, due to the presence of silica protrusions on the stems, the *Equisetum* species, which have been used for polishing metallic plates and tin products, is one such recent source used to produce nano silica and published reports are available in respect of *Equisetum hyemale*, [5,38,39]. This is because the species of *Equisetum* are known as plants with high accumulation of silicon ('biogenetic silica'). It has also been well established that this species contains salts/minerals of potassium, magnesium, calcium, phosphorous, sodium and aluminum as its constituents, having more than 10% of inorganic constituents, as well as phenolics, flavonoids, among others. It is also well established the possibility of silicon concentrations reaching about 25% of its dry weight in these species and 25 wt.% of silica has been found to have been accumulated in the 'knobs in the amorphous form and as a thin layer below the cuticle [5,39,49]. It is also reported that silica deposits in plants can be present in the cell walls, in the cells and in the intercellular space [5,38], as a means to absorb the salicylic acid from the soil [5,49] and to transport it to the interior of the plants. Distribution of different types of silica in the *Equisetum hyemale* species has been determined by confocal Raman microscopy and Scanning Electron Microscopy (SEM) with energy dispersive (EDAX) attachment [5,38].

Based on the above background about the importance of nano silica in many applications and of the need for renewable resources to produce these, particularly from those with higher silica content, another plant belonging to the Equisetaceae Family, the *Equisetum arvense* (*E. arvense*-Field Horsetail) is considered. To the best knowledge of the authors, there have been no published reports on the use the plant *Equisetum arvense* to produce nano particles of silica. Hence, this study, forming the first, on this plant was taken up with the objective of producing nano silica from this source and to find a suitable use for the same. Accordingly, this paper presents an attempt to develop a cheap, efficient production method of Nano silica of high purity using a renewable *Equisetum arvense* plant and its characterization.

It may be noted that unlike other type of plants such as banana, kenaf, pineapple leaf, sisal, *Phormium tenax* (harakeke), mengakuang, mulberry whose stems / barks/ fibers have been used for the preparation of nano silica, leaves or stem or root of *Equisetum arvense* plant cannot be considered separately for this purpose. This is because, it is economically not viable to industrially exploit (to construct bio refinery) the plant (*E. arvense*) due to the need to separate the stem and roots of this plant. Besides, this *gramineae* (subshrub of tropical America) presents a morphology in which the leaves to stem ratio is small. Besides, the root should remain in soil to avoid excessive nutrient and export of carbon from the soil that is important to keep the soil fertility after many plantation cycles. Hence this cannot be a source for producing nano silica. On the other hand, many of the other plants mentioned above (banana, pineapple, etc) are of shorter life and after producing the fruits, they could be used for the preparing nano silica.

Also, cost of this nano silica could be lower than the commercial ones available in view of the raw material used (plant material) and low energy requirement of the process followed in this study. Further studies, including the use of the nano silica produced, will be reported in subsequent publications.

## Experimental

### Materials

The samples of *Equisetum arvense* L. shown in Figure 1 were obtained from the experimental plantation of EMBRAPA Forestry, located in the municipal district of Colombo, PR, Brazil.

### Methods

**Sample preparation:** In the present study, nano silica was obtained after calcination of the treated biomass as it is known that the quality of the produced silica depends on the treatments used to obtain them [29,50].

In order to obtain high purity nano silica particles ( $\text{SiO}_2$ ) from the above source, different chemical and thermal methods were carried out. First, 500 g of the sample was washed using deionized water to remove any impurities from the soil sticking on its surface and other possible pollutants. Next, in order to remove metallic sludges that may affect the purity of the silica produced, if any were present, the sample was subjected to chemical treatment by washing it several times with 2000 mL solution of deionized water containing 2% HCl acid contained in a flask for about 2 h in a vertical autoclave at a pressure of 1.5 kgf/cm<sup>2</sup> (15000 kgf/m<sup>2</sup>) and temperature of about 393 K. Effectiveness of these two treatments was tested by subjecting the samples to one or two cycles of washing. After this, the samples were washed with deionized water until the required pH (acid or neutral) was obtained as reported elsewhere [51-53] and they were then dried in a hot air oven kept at 376 K to remove the residual water. It may be noted that required values of pH are 7 for neutral and 4 for acid. In fact, it is reported that pH influences the quality of the obtained material [51]. This is also observed in the present study.

The dried material was then taken in a porcelain container, made into powder using ceramic balls of varying diameters (10-20 mm) through a Servitech ball mill, which rotates horizontally. Rotation of the ball mill was kept at 54 RPM for 24 h with a view to get powder samples of size 2.5 mm. The container was filled 20% with the sample and about



Figure 1: *Equisetum arvense* L. (CAVALINHA).

50% with the ball mill, where the sample slightly covered the balls. The ceramic balls used with the grinders were of variable diameters between 10 and 20 mm. This procedure was followed for all the samples prepared in this study. Then, the acid washed samples in powder form, kept in crucibles in order to get uniform heating, were subjected to thermal treatment by calcining them at three different temperatures (773 K, 823 K and 873 K) for about 2 hrs. Selection of temperature for calcination was based on an earlier reported range to get the best properties [5]. The various treatments used and the obtained samples with their designations are listed in Table 1.

Sample T1 represents the oven dried powdered sample of *Equisetum arvense* L., while the samples T2, T6 and T10 were acid washed, but not calcined. On the other hand, the remaining samples (T3-T5, T7-T9, T11-T13) represent the number of acid washings (1 or 2) along with respective pH (neutral or acid) obtained after each wash and the temperature of calcination given to these samples. There are reports following similar methodology [51,52].

**Characterization:** Obtained nano silica particles were characterized for their density, Specific Surface Area (SSA), chemical structure by Fourier Transform Infrared Spectroscopy (FTIR), morphology by both Scanning and Transmission Electron Microscopy (SEM / TEM) and structural aspects by X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF). The density of the samples was determined using a pycnometer based on Archimedes' principle, using water as the solvent medium.

The specific surface area was measured with NOVA<sup>®</sup> 1200e Quantachrome BET equipment (Model I) using nitrogen atmosphere. For this purpose, the sample was taken in a glass 'U' tube and then purged with a flux of nitrogen at 523 K for 2 h. Then, the process of adsorption and desorption was followed by keeping the sample tube immersed in liquid nitrogen (77° K) at the temperature in which the nitrogen gas is adsorbed by the sample. After this, the tube was taken out from the liquid nitrogen atmosphere and heated in air to enable the nitrogen to desorb from the sample, resulting in isotherms. Subsequently, well known BET model was followed, where multilayer adsorption of nitrogen on to a surface allows determining the surface area. The portion of isotherm for this silica is classified as Type IV as per IUPAC 1984. Then, the average size of particles D (BET) was calculated based on the well known measurement of BET using the Equation (1), considering the isometric approach for the particles:

$$D \text{ (BET)} = 6 / \rho \times \text{SSA (BET)} \quad (1)$$

Where  $\rho$  is the density ( $\text{g}/\text{cm}^3$ ) of the material and SSA (BET) is the specific surface area ( $\text{m}^2/\text{g}$ ), as measured by BET. Kreyling et al. [54] in their study of nano materials have defined the volume of the specific surface area (VSSA) as given in Equation 2 below, wherein a direct relationship exists between the specific surface area (SSA) determined by BET method and the density of the material:

$$\text{VSSA (m}^2 \cdot \text{cm}^{-3}) = \text{SSA (m}^2 \cdot \text{g}^{-1}) / \rho \text{ (g} \cdot \text{cm}^{-3}) \quad (2)$$

With this, their definition of nano material is one which has VSSA  $\geq 60 \text{ m}^2 \cdot \text{cm}^{-3}$ .

The structural aspect of particles having lower SSA was determined with a Philips / Panalytical X-ray equipment (I Model PW 2400) using Cu-K $\alpha$  radiation at room temperature, while for the samples having larger SSA (T11), Shimadzu (I Model XRD-6000) equipment was used. The diffraction angle ( $2\theta$ ) was varied from 10-70° at 0.02° interval.

For the morphological characterization of the obtained nano silica particles, both Scanning and Transmission microscopes (SEM /

TEM) were used. For the surface study of the obtained particles, JEOL scanning electron microscope (JMS-6360LV) was used. The samples were prepared for this first by dispersing the particles in a solution diluted with isopropyl alcohol using a small glass tube with rubber holder to get drops on to the samples and then evaporating the alcohol. Then, the samples were coated by a thin gold film. Moreover, the internal structure of the Nano silica particles was determined using a JEOL transmission electron microscope (Model: JEM 1200EXII).

## Results and Discussion

The results obtained in this study are presented and discussed below in terms of the effect of the processing method (acid washing/pH and temperature) on the color of the product obtained, diameter, surface area and chemical composition.

The macro photographs of some representative samples of nano silica particles obtained in this study are shown in Figures 2a-2c, while Table 2 shows the values of Specific Surface Area (SSA), average size of the particles (D BET) as well as the color of the samples observed visually. It may be noted that the values for the main treatments are shown in bold, while the others in normal fonts represent secondary treatments due to changes in the temperature.

### Effect of acid washing

Sample T1, which is the oven dried powdered sample of *Equisetum arvense* L., is shown in Figure 2a. This silica has predominantly gray color and contains small quantity of white ash, suggesting the presence of still existing carbonaceous (organic) matter on calcination. Figure 2b, on the other hand, represents the samples T2, T6 and T10, which are acid washed, but not subjected to calcination. The color of silica is brown in this case, suggesting a huge amount of organic matter, as observed in the sample without acid washing (T1). This is similar to that observed earlier in the silica obtained from *Equisetum hyemale*, belonging to same family of Equisetaceae, which was also subjected to acid wash or further calcined up to 673 K [5]. Finally, Figure 2c, representing the samples T3, T5, T7, T9, T11 and T13 (acid washed and subjected to calcination at different temperatures) shows silica of white color, suggesting complete absence of all organic matter after calcination. These results clearly indicate the effects of acid washing and calcination on the color of the silica obtained. Also, they are in agreement with earlier reports on amorphous nano silica obtained using rice husk through acid washing followed by calcining at higher temperatures (973K-1073 K) than those used in the present study [6,37], and also of Nano silica obtained from *Equisetum hyemale* calcined between 773-1023 K [5].

Table 2 shows that the specific surface area values of the silica nanoparticles produced varied between the lowest of about 217  $\text{m}^2/\text{g}$  to the highest value of 331  $\text{m}^2/\text{g}$  for the samples subjected to both acid washing and calcination. These values are higher than those reported for silica nanoparticles produced following the same procedure, but using rice husk (81  $\text{m}^2/\text{g}$  and 120  $\text{m}^2/\text{g}$  - 235  $\text{m}^2/\text{g}$ ) [37,55] as well as that of commercial micro silica (15-28  $\text{m}^2/\text{g}$ ) and silica fume [55] (<http://www.norchem.com/pdf/silica-fume-data-sheet.pdf>) but, lower than that obtained in *Equisetum hyemale* (>400  $\text{m}^2/\text{g}$ ) [38]. These high values of SSA can be attributed to the removal of alkaline and alkaline earth elements from the biomass, leaving silicon compounds unchanged by acid washing. Calcination has burnt the carbon compounds into carbon monoxide and water and degraded the silicon compounds into silica. This silica is bio-mimetic of lignin shape and is of porous nano metric particles. These nano silica particles may condense into

Sample Designations	Acid Washing Cycles	pH	Temperature (K)
T1	-	-	773
T2	1	7	-
T3	1	7	773
T4	1	7	823
T5	1	7	873
T6	2	4	-
T7	2	4	773
T8	2	4	823
T9	2	4	873
T10	2	7	-
T11	2	7	773
T12	2	7	823
T13	2	7	873

Table 1: Various treatments used to produce Nano silica from *Equisetum arvense* L.

Sample Designations	SSA (m <sup>2</sup> /g)	D BET nm	Color
T1	54.00 ± 0.80	50.28	Gray
T2	74.08 ± 0.32	36.65	Brown
T3	296.40 ± 0.55	9.16	White
T4	274.64 ± 0.60	9.89	White
T5	230.63 ± 0.27	11.77	White
T6	69.57 ± 0.96	39.03	Brown
T7	250.49 ± 0.48	10.84	White
T8	228.03 ± 0.76	11.91	White
T9	216.91 ± 0.16	12.52	White
T10	83.45 ± 0.93	32.54	Brown
T11	330.63 ± 0.68	8.21	White
T12	296.40 ± 1.02	9.16	White
T13	250.73 ± 0.45	10.83	White

Table 2: Values of specific surface area obtained by BET, average size of the particles (D BET) and color of the samples

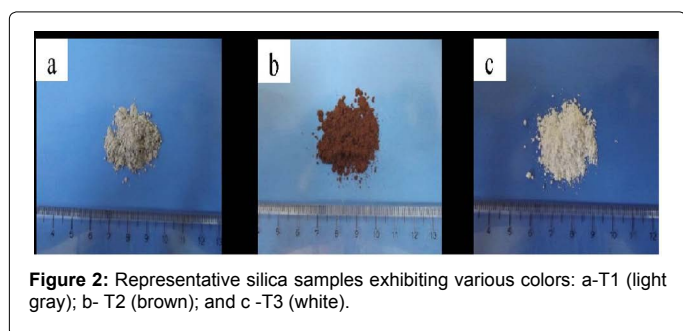


Figure 2: Representative silica samples exhibiting various colors: a-T1 (light gray); b- T2 (brown); and c- T3 (white).

micrometrical particles depending on temperature of calcining and / or liquid phase sintering. Glassy phase can be formed at low temperatures in the presence of alkaline earth and alkaline atom metals.

However, SSA values of samples of T2, T6 and T10 varied between 69 m<sup>2</sup>/g -83 m<sup>2</sup>/g, the highest value in this range, which is similar to that observed for Nano silica obtained from rice husk as mentioned above, but with calcination [37]. However, the increase in values from about 74 m<sup>2</sup>/g to about 83 m<sup>2</sup>/g can be understood as being due to the increased cycle of acid washing, though the lower value of sample T6 may be due to lower value of pH.

Furthermore, T3, T4 and T5 resulted in nano silica particles with SSA values of about 296 m<sup>2</sup>/g, 275 m<sup>2</sup>/g and 231 m<sup>2</sup>/g, respectively.

It should be noted that these samples were subjected to one cycle of acid washing, but at different temperatures. All these also had similar pH value of 7. On the other hand, samples T7, T8 and T9 showed somewhat higher SSA values (216 m<sup>2</sup>/g -250 m<sup>2</sup>/g) despite the fact that they could be easily handled, as experienced during powdering in the ball mills. This could be due to low pH values (pH=4) compared to T3, T4 and T5 (pH=7). This suggested that the pH of the sample affects the SSA of the resulting silica particles.

Finally, the samples T13, T12 and T11 showed nano silica with SSA values of about 251 m<sup>2</sup>/g, 296 m<sup>2</sup>/g, and 331 m<sup>2</sup>/g, respectively. These samples were also subjected to acid washings and calcined at the same temperatures as T3, T4 and T5 but acid washed twice. All of these were of white color, having the same pH, but calcined at different temperatures. This suggests that calcination temperature determines the SSA and color, while the number of acid washes and high pH are kept constant. Furthermore, it should also be noted that lowest calcining temperature used was 773 K, which produced nano silica of white color with the highest SSA (Sample 11), while increased calcining temperature decreased the values of SSA even when the cycle of acid washing was kept constant (Samples T7-T9) or the pH was kept constant while changing the number of acid washings (Samples T3-T5). Similar observations have been reported by Sapei [5], who used *Equisetum hyemale* samples with the range of calcining temperatures from 623 K to 973 K, but obtained the best result only at 773 K. The decrease in the values of SSA with the increasing calcining temperature may be understood as due to the collision that the surface of the particles undergo along with their agglomeration at higher temperatures. Higher temperature increases the sintering rate of Nano silica, leading to an Oswald ripening process where, due to inter particle diffusion, the smaller particles would become even smaller, while the larger ones continue to grow similar to well known Ostwald ripening during liquid phase sintering. This results in an increase of the particle size.

From the above, it becomes evident that acid washing is one of the major steps influencing the process to obtain nano silica particles from biomass resource, as is evident from the results of samples T2, T6 and T10. The next step is the number of cycles of acid washing that influences the SSA resulting in Nano silica, as is evident from the results of samples T2 (subjected to one cycle of acid washing- showing a value of 74.08 m<sup>2</sup>/g) and T10 (subjected to two cycles-showing the value of 83.45 m<sup>2</sup>/g). This indicates that increasing the cycle of acid washing even just once resulted in an increase in the SSA approximately by 10 m<sup>2</sup>/g. The next determining step to obtain white color nano silica with higher SSA is the calcining temperature. Lower temperatures seem to have a higher influence in this. These, along with the pH of the material, finally dictate the quality of nano silica produced from the plant material used in this study. Such effects of acid washing and pH can be understood as follows.

When the plant sample was washed with 2% HCl, it not only removed the inorganic substances such as K and Ca, but it might have also dissolved the pectins and hemicelluloses in the plant sample used [56]. Also, during this process, the amorphous cellulose might have been dissolved [57] along with the possibility of a partial hydrolysis of crystalline cellulose, thus decreasing the degree of polymerization called 'phenomena of hydrocellulose' whereby the swelling of cellulose takes place [58]. Furthermore, due to the action of HCl, about 95% of inorganic and 65% of organic wastes are removed, leaving cavities in the structure of the sample [5,39]. Additionally, with acid washing, a porous material would be obtained, and such highly porous material subjected to higher temperatures would remove the remaining organic

matter, thus leading to increased SSA [35].

It can therefore be concluded that the pH and the number of acid washes, combined with low calcining temperature, influence the purity and high surface area of the resulting Nano silica produced with *Equisetum arvense* L.

Moreover, it can be seen that sample T1 is solely burnt plant material and this product is of gray color, suggesting the presence of some impurities in agreement with the earlier observation that the color of carbonaceous material resulting from the burning of lignocellulosic materials is due to the incomplete decomposition of lignocelluloses [6].

The purity of the sample can be judged not only by the value of SSA, but also by its color. This is evident from the silica obtained in this study, where the two extreme ends of the samples are considered. Sample T1 is only charred plant material with a gray color, while sample T11 is twice acid washed and then calcined at the lowest temperature. While the latter exhibited the best SSA value along with the white color, the former showed the lowest SSA and gray color. This is further corroborated by the X-ray fluorescence studies giving the chemical composition of these Nano particles, which is shown in Table 3.

The table above shows that the acid wash of *Equisetum arvense* L. samples certainly has a profound effect in reducing the alkaline and alkaline earth ions. Also, there is considerable reduction in some of the elements in these samples, particularly of Ca, K, Mg and P, which affect the SSA. Furthermore, it also shows that silica obtained by just burning (Sample T1) shows high amounts of impurities/ash (2.19%), while the sample subjected to both acid washing and calcination (T11), shows the highest content of SiO<sub>2</sub> (93.5%). A high amount of ash observed in sample T1 is due to the presence of carbonaceous material, as already evidenced by the color of silica obtained.

Figures 3a-3b shows the scanning electron micrographs of high purity silica nano particle agglomerates obtained from sample T7 and Figure 3c that from sample T11, while Figure 3d is the transmission photograph of the high purity silica obtained from sample T11 in this study.

Figures 3a-3c shows that obtained nano particles are compact. Furthermore, the agglomerate size observed seems to be about 300 nm, indicating that it was not possible to separate them into individual particles, with the average size (diameter of these particles) of approximately 8 nm in agreement with the nitrogen sorption experiment mentioned earlier. Similar observation of agglomerated nano silica particles have been observed by other researchers also [59,60]. Another interesting observation from Figures 3a and 3b is that the particles obtained from sample T7, showed the presence of some joined particles, [agglomeration marked by the arrow in Figure 3a], which was not the case with sample T11 as seen in Figure 3b, showing the fine nature of the powder.

It seems that the agglomeration is characteristic and peculiar for this type of material, suggesting that this occurs in samples of low pH of acid washed samples, in agreement with the observation that samples with pH below 5 would be formed under positive loads, probably favoring the agglomeration of silica.

Figure 4 shows the X-ray diffraction pattern of obtained high purity amorphous silica. It can be seen that the highest broad scattering band is observed at 2θ value of about 22°, with no Bragg diffraction peaks related to amorphous silica, in agreement with the earlier observation of Abreu [61] on silica obtained from rice husk and that reported by Freitas et al. [62] on silica obtained from rice husk and endocarpy of

babassu coconut, attributing this to amorphous silica. However, Liou and Wu [55] have observed this peak at 2θ =22.5° for nano silica obtained from acid washed and water-washed rice husk. This also suggests that the silica structure is neither affected by either the acid and water washings or the calcination treatments used in the present study, in agreement with earlier reports mentioned above on nano silica obtained from rice husk [51,52].

Further studies carried out on the use of the nano silica produced and characterized here for treating wood veneers for improved performance in comparison to other conventional treatments through prediction and experiments are under preparation for publication.

## Conclusions

It is possible to obtain nano particles of silica from *Equisetum arvense* (horse tail) efficiently by adopting suitable chemical and thermal treatments.

Acid wash of samples of *Equisetum arvense* L with 2% HCl not only solubilizes, but also removes some elements present in the plant material during dissolution, as evidenced in XRF studies. This indicates that HCl treatment before any calcination is very advantageous as it provides a high purity raw material from which to produce Nano silica.

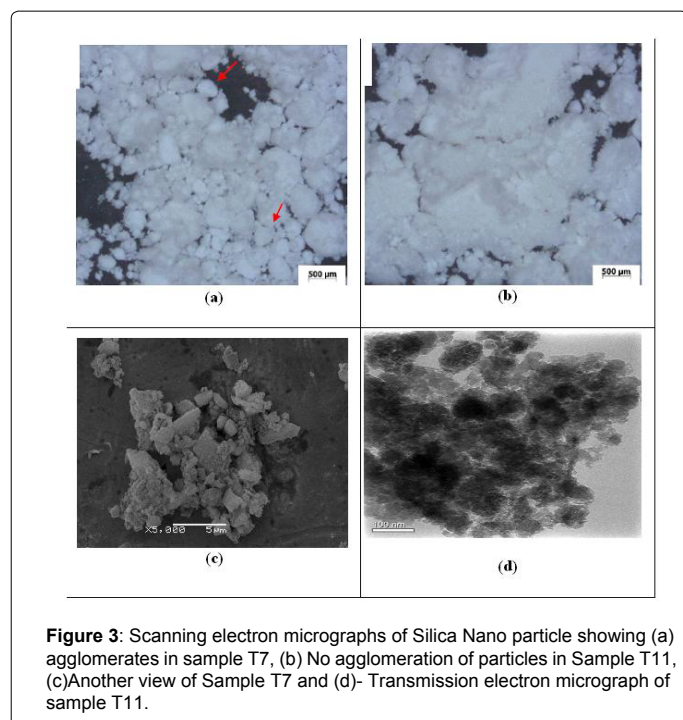
The combination of two cycles of acid wash and calcination at 773 K gave the best Nano silica particles with the highest specific surface area of ~300 m<sup>2</sup>/g and of white color. High purity is associated not only with the color of the silica material obtained, but also with the retention of the amorphous nature despite combined effects of both chemical and thermal treatments used.

The bio-silica obtained in this study from the *Equisetum arvense* may be a potential candidate as raw material for various industries, mainly in the ceramic industry and building sector, as well as in various other applications mentioned earlier. The application may also include substitution of the activated or micro silica in the production of high performance concrete.

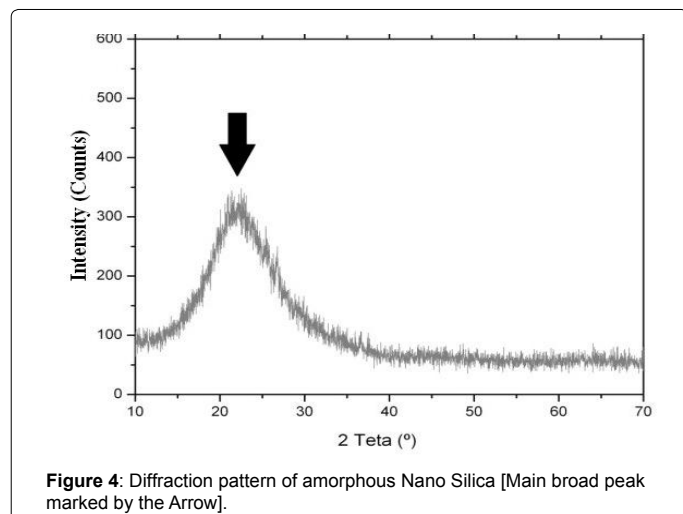
Oxides	Sample T1(%)	Sample T11 (%)
SiO <sub>2</sub>	59.6	93.5
CaO	15.2	1.8
SO <sub>3</sub>	2.2	0.9
K <sub>2</sub> O	11.0	0.6
MgO	4.9	0.3
Al <sub>2</sub> O <sub>3</sub>	0.2	0.5
P <sub>2</sub> O <sub>5</sub>	2.5	0.3
Fe <sub>2</sub> O <sub>3</sub>	0.2	0.1
ZnO	0.1	<0.1
TiO <sub>2</sub>	0	<0.1
CuO	<0.1	<0.1
SrO	0.1	0
MnO	0.1	0
BaO	0.1	0
ZnO	0.1	0
CuO	<0.1	0
Ash	2.19	1.76

T1: Powdered plant sample and burnt at 500°C; T11: Plant material with twice acid washed and calcined at 500°C and pH 7

**Table 3:** Chemical Composition of *Equisetum arvense* L. samples T1 and T11 obtained by X-ray Fluorescence after chemical treatment



**Figure 3:** Scanning electron micrographs of Silica Nano particle showing (a) agglomerates in sample T7, (b) No agglomeration of particles in Sample T11, (c) Another view of Sample T7 and (d) Transmission electron micrograph of sample T11.



**Figure 4:** Diffraction pattern of amorphous Nano Silica [Main broad peak marked by the Arrow].

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