Introduction

1.1 Natural of silica:

The name silica comprises a large class of products with the general formula SiO_2 or $SiO_2.xH_2O$. Silica is a naturally occurring material in minerals, such as quartz and flint, and in plants such as bamboo, rice and barley. Most of the silica used in chemical applications however, has a synthetic origin. In its natural form it mostly occurs as a crystalline phaseVarious phases may be formed, depending on temperature, pressure and degree of hydration Silica, SiO_2, is an in-volatile solid and occurs in many different forms, nearly all of which possess 3-dimensional structures constructed from tetrahedral SiO_4 building blocks (Vanstant, et-al, 1968). Each unit is connected to the next by sharing an oxygen atom to give Si-O-Si bridges.

In all forms of silica, the Si-O bond length is 160 pm and the Si-O-Si bond angle is 144°. By heating silica under very high pressure, a rutile form containing 6-coordinate Si is formed in which the Si-O bond length is 179 pm.

1.2 Occurrence:

Even though it is poorly soluble, silica occurs widely in many plants. Plant materials with high silica phytolith content appear to be of importance to grazing animals, from chewing insects to ungulates. Studies have shown that it accelerates tooth wear, and high levels of silica in plants frequently eaten by herbivores may have developed as a defense mechanism against predation.

It is also the primary component of rice husk ash, which is used, for example, in filtration and cement manufacturing (http://en.wikipedia.org/wiki/Silicon_dioxide).

Silicification in cells has been common in the biological world for well over a billion years. In the modern world it occurs in bacteria, single-celled organisms, plants, and animals (invertebrates and vertebrates). Prominent examples include:

- Tests or frustules of diatoms and Radiolaria.

- Silica phytoliths in the cells of many plants, including Equisetaceae, practically all grasses, and a wide range of dicotyledons.

- The spicules forming the skeleton of many sponges.

It is unclear in what ways silica is important in the nutrition of animal. This field of research is challenging because silica is ubiquitous and in most circumstances dissolves in trace quantities only. All the same it certainly does occur in the living body, leaving us with the problem that it is hard to create proper silica-free controls for purposes of research. This makes it difficult to be sure when the silica present has had operative beneficial effects, and when its presence is coincidental, or even harmful. The current consensus is that it certainly seems important in the growth, strength, and management of many connective tissues. This is true not only for hard connective tissues such as bone and tooth but possibly in the biochemistry of the sub-cellular enzyme-containing structures as well (http://en.wikipedia.org/wiki/Silicon_dioxide, 27/9/2014 at10:22PM).

1.3 Names of silica:

The IUPAC *name is* silicon dioxide. Other generic names are quartz, silicic oxide, silicon (IV) oxide and crystalline silica (http://en.wikipedia.org/wiki/Silicon_dioxide).

1.4 Classification of Silica:

At atmospheric pressure the anhydrous crystalline silica may be classified to the following phases, according to the temperature: (Vanstant, et-al, 1968).

Quartz $\xrightleftharpoons{1143k}$ Tridymite $\xrightleftharpoons{1743k}$ Cristobalite
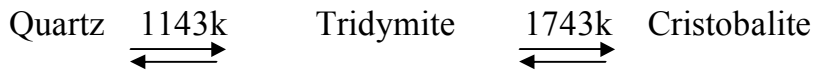
At 1973 K cristobalite is transformed to amorphous vitreous silica glass. The crystalline form involves a high degree of ordering in a dense structure. The active surface, which may participate in any chemical or physical interaction, is limited to the external surface of the crystalline particles. The specific surface area therefore is similar to the geometric surface.

Amorphous silica occurs in various forms. According to the application, fibres, sheets, sols, gels and powders may be fabricated. A clear view upon the properties of all amorphous forms can be obtained from the process used for their preparation (Vanstant, et-al, 1968).

A main feature of interest in this work is the porosity of the amorphous silica forms. Porosity introduces a large surface area inside the silica particles. As inter-phase processes require a large surface/mass ratio, amorphous silicas are far more interesting for chemical and physical applications than their crystalline counterparts (Vanstant, et-al, 1968).

Another type of classification is based on the source of silica: (Barby, 1979).

- Natural Silica: Has specific surface area similar to their geometric surface.

- Synthetic Silica(mostly amorphous) : Surface area ,pore volume, pore size and particle size are to some extent independently Controllable(commercially interesting(, and it has four types:

- Colloidal Silica(silica sole): Stable dispersion or sole of discrete particles of amorphous silica.

- Silica gels: Coherent, rigid, 3D net work of contiguous of colloidal silica ,and it has three types:

- Hydro gels: Silica gel, in which the pores are filled with the cross Bonding Liquid (water).

- Xerogels: A gel from which the liquid medium has been removed resulting in a compressed structure and a reduced porosity.

- Aero gels : Special form of xerogel from which the liquid has been removed in such away as to prevent any collapse or change in the structure as liquid is removed. Age wit water-collapsible microspores a judged by direct porosimetry .

- Pyrogenic silica : Silica made at high temperatures, and it has three types:

- Aerosils: flame hydrolysis products of silicon tetra chloride; very pure materials.

- Arc Silica : made by the reaction of high purity sand .

- Plasma silica : ultra fine silica powder , made by the direct volatilization of sand in aplazma jet.

- Precipitates: made by the precipitation of the Silicic acid solution.
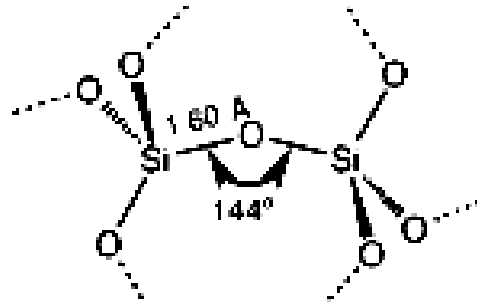
1.5   STRURCTUR OF SILICA:

Fig. 1.1: The Structural motif found in α-quartz, but also found in almost all forms of silicon dioxide.

(wikipedia,2014).

1.6   Physical PROPERTIES:

Table 1.1: the physical properties of silica powder (Wikipedia, 2014)

Molecular formula	SiO_2
Molar mass	60.08 g/mol
Appearance	Transparent crystals
Density	2.648 g·cm^{-3}
Melting point	1,600 to 1,725 °C (2,912 to 3,137 °F; 1,873 to 1,998 K)
Boiling point	2,230 °C (4,050 °F; 2,500 K)

1.7 Solubility in water:

The solubility of silicon dioxide in water strongly depends on its crystalline form and is 3–4 times higher for silica than quartz; as a function of temperature, it peaks at about 340 °C. This property is used to

grow single crystals of quartz in a hydrothermal process where natural quartz is dissolved in superheated water in a pressure vessel that is cooler at the top. Crystals of 0.5–1 kg can be grown over a period of 1–2 months. These crystals are a source of very pure quartz for use in electronic applications (http://en.wikipedia.org/wiki/Silicon_dioxide, 27/9/2014 at10:22PM).

1.8 Chemical properties of Silica:

Silicon dioxide is an acidic oxide which although insoluble in water ,dissolves in aqueous alkali , forming the silicate anion.

Silica is not attacked by acids other than HF, forming $[SiF_6]^{2-}$ and $[SiF_5]^{-}$ Ions. Normal silica is only very slowly attacked by alkali, however, by fusing SiO_2 and metal hydroxides, oxides or carbonates and silicates are readily formed. (http://en.wikipedia.org/wiki/Silicon_dioxide, 27/9/2014 at10:22PM).

1.8. A. Chemical Reaction:

Silica is converted to silicon by reduction with carbon.

Fluorine reacts with silicon dioxide to form SiF_4 and O_2 whereas the other halogen gases (Cl_2, Br_2, I_2) are essentially un reactive.

Silicon dioxide is attacked by hydrofiuoric acid(HF) to produce hexafluorosilicic acid:

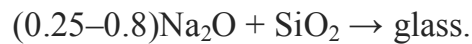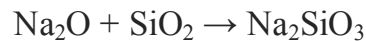$$SiO_2 + 6\,HF \rightarrow H_2SiF_6 + 2\,H_2O.$$
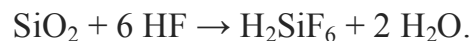
HF is used to remove or pattern silicon dioxide in the semiconductor industry.

Silicon dioxide dissolves in hot concentrated alkali or fused hydroxide, as described in this idealized equation:

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O.$$
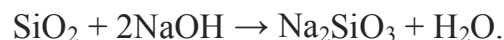
Silicon dioxide reacts with basic metal oxides (e.g. sodium oxide, potassium oxide, lead(II) oxide, zinc oxide, or mixtures of oxides formingsilicates and glasses as the Si-O-Si bonds in silica are broken successively). As an example the reaction of sodium oxide and SiO_2 can produce sodium orthosilicate, sodium silicate, and glasses, dependent on the proportions of reactants:

$$2\ Na_2O + SiO_2 \rightarrow Na_4SiO_4$$

$$Na_2O + SiO_2 \rightarrow Na_2SiO_3$$

$$(0.25–0.8)Na_2O + SiO_2 \rightarrow glass.$$

Examples of such glasses have commercial significance, e.g. soda-lime glass, borosilicate glass, lead glass. In these glasses, silica is termed the network former or lattice former.

Silicon dioxide reacts with elemental silicon at high temperatures to produce SiO:

$$SiO_2 + Si \rightarrow 2\ SiO$$
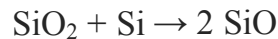
(http://en.wikipedia.org/wiki/Silicon_dioxide, 27/9/2014 at10:22PM).

1.8. B Alkali–silica reaction:

The alkali–silica reaction (**ASR**) is a reaction which occurs over time concretein between the highly alkaline cement paste and reactive non-crystalline (amorphous) silica, which is found in many common aggregates.

The ASR reaction is the same as the pozzolanic reaction, which is a simple acid-base reaction between calcium hydroxide, also known as Portlandite, or ($Ca(OH)_2$), and silicic acid (H_4SiO_4, or $Si(OH)_4$). For the sake of simplicity, this reaction can be schematically represented as following:

$$Ca(OH)_2 + H_4SiO_4 \rightarrow Ca^{2+} + H_2SiO_4^{2-} + 2\,H_2O \rightarrow CaH_2SiO_4 \cdot 2\,H_2O$$

This reaction causes the expansion of the altered aggregate by the formation of a swelling gel of calcium silicate hydrate (C-S-H). This gel increases in volume with water and exerts an expansive pressure inside the material, causing spelling and loss of strength of the concrete, finally leading to its failure.

ASR can cause serious expansion and cracking in concrete, resulting in critical structural problems that can even forces the demolition of a particular structure.

The mechanism of ASR causing the deterioration of concrete can be described in four steps as follows:

- The alkaline solution attacks the siliceous aggregate, converting it to viscous alkali silicate gel.

- Consumption of alkali by the reaction induces the dissolution of Ca^{2+} ions into the cement pore water. Calcium ions then react with the gel to convert it to hard C-S-H.

- The penetrated alkaline solution converts the remaining siliceous minerals into bulky alkali silicate gel. The resultant expansive pressure is stored in the aggregate.

- The accumulated pressure cracks the aggregate and the surrounding cement paste when the pressure exceeds the tolerance of the aggregate.

(Wikipedia, 2014)

1.8. C Self-catalyzed water reactions with silica:

Silica (SiO2) is one of the most abundant minerals on the Earth's surface, and is an important technological material. In its applications, the role of water and how it changes the

Properties of silica are very important. Here first principle Molecular dynamics simulations are   Reaction between water and silica could occur through hydrogen transfer at low temperature

Addition of extra water molecules can reduce the activation energy of the hydrolysis reaction.

Water stabilizes the transition states through hydrogen bonding and participates in hydrogen transfer (Sole, et-al, 1964).

1.8. D: Investigation of the states of water and OH groups on the surface of silica:

Silica powders are widely used in industry such as fillers, catalysts, adsorbents, chromatographic, agents, and so on(Mack, et-al, 2006), (Wn, et-al, 2005), (Ghosh, et-al, 2008), (Stöderg, et-al, 2007).

Because SiO2 powders have high free energy, they are easily absorbed by water under room temperature which forms, silica powders may be made of siloxane group(Si–O–Si) and several forms of silanol groups (Si–OH), (Zhuravler, et-al, 2000), Both the water and silanol groups on surface may affect the reactions used to modify the surface with alkyl silanes. Surface water and OHgroups would thus play a role in the selectivity and thermodynamics in the process of surface modification or self-assembly on silica surface. Therefore, the investigation of water and OH groups would be of interest in understanding modification of silica with affinants.It has been reported that both "chemisorption" and "physical adsorption" water exist on the surface of silica Kellum, et-al, 1967), (Muellar, et-al, 2003), (Shioji,et-al, 2007), (takei, et-al). Analysis

of chemisorption and physical adsorption requires that a differencebe made between SiOH groups and physically bound or hydrogen bonded water on the surface. It is difficult, however, to distinguish between adsorbed water and actual surface hydroxyl groups. To determine the surface structure (especially OH groups) of powders, infrared (IR) spectroscopy, Raman spectroscopy, and thermogravimetric analysis (TGA), aswell as chemical methods such as titration and nuclear magnetic resonance (NMR) are used(Gilpin, et-al, 1997), (Crupi, et-al, 2008). Fouriertrans form infrared (FT-IR) spectroscopy is most commonly applied formonitoring the surface hydroxylation of silica(Ramos, et-al, 1998) . Furthermore,the thermal analysis coupled with other methods is often used to study dehydroxylation and to estimate the number of OH groupson the surface because it does not requires samples that are hard to prepare(Mueller, et-al, 2003) .The goal of this work was to evaluate the properties of water and OH groups associated with the surface of amorphous silica. After the amorphous silica was heated to 873K to dehydrate, it was dehydrated to different degrees with heat treatment at 323, 473, 673,873, 1073 and 1273 K. Thermal analysis including thermo gravimetry(TG) and differential scanning calorimetry (DSC) combined withFT-IR spectroscopy was used for studying the states of water andOH groups on the surface of nanosilica .
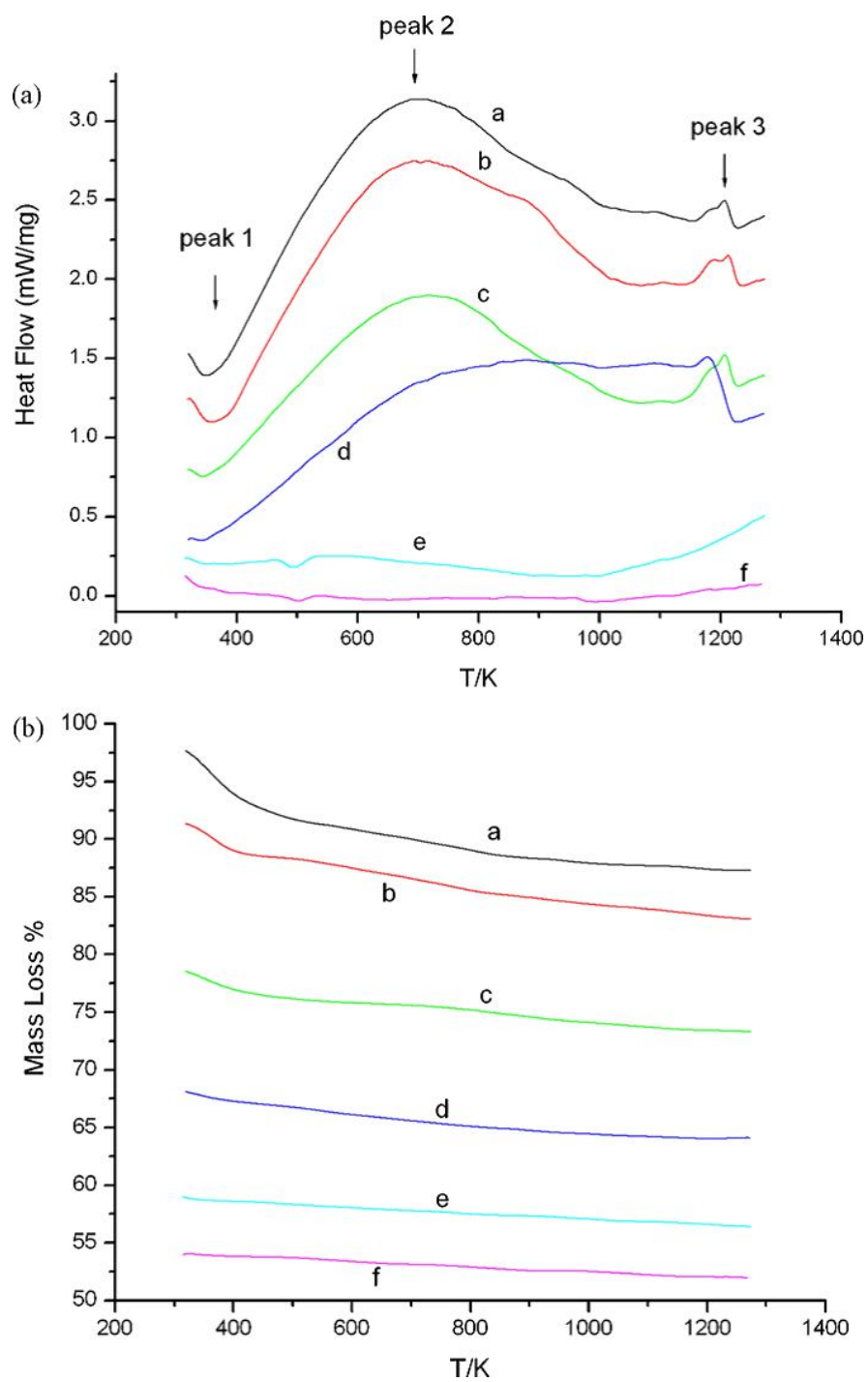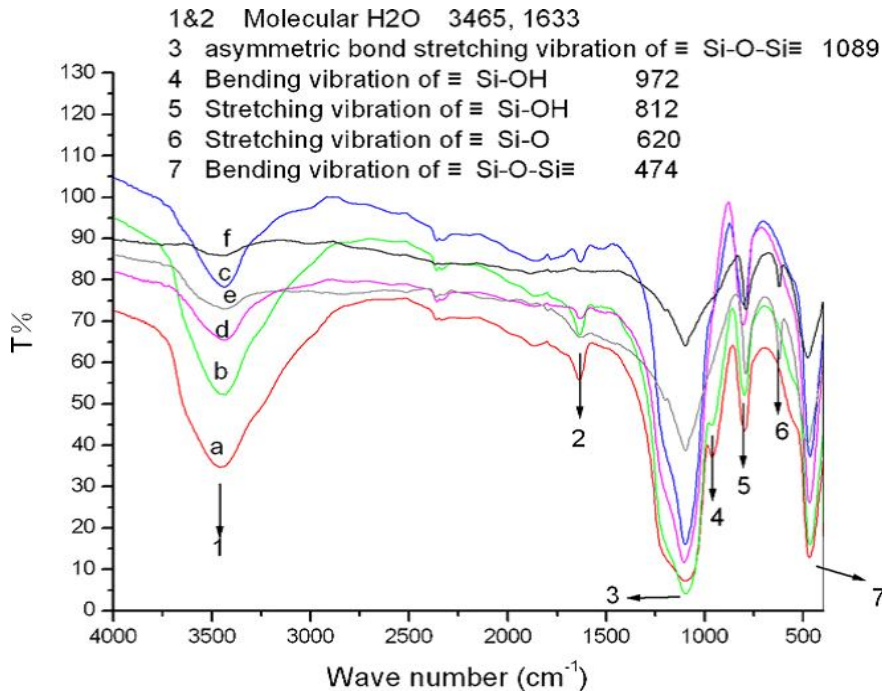
Fig 1. 2.curves of the amorphous nanosilica .

Fig 1. 3. FT-IR spectra of the amorphous nanosilica

The DSC and TG curves were obtained by continuous heating ofthe silica with a definite temperature rate shown in Fig. 2(a) and(b), respectively.. The FT-IR spectra curves were shown in Fig. 3.Both the silanol groups and physically bound or hydrogen bonded water exists on the surface of silica. The chemical bond of silanol and weak adsorption physically or hydrogen-bond are different, so water on the surface could be dehydrated under different temperature. In Fig. 2(a), the first peak appeared at about 343Kfor samples a–c. This suggests that the physically adsorbed water was removed mainly at 343 K. As for sample d, a small thermal change at 343K could be observed, but could not be observed for samples e and f. The results suggest that the physically adsorbed water was removed nearly completely between 873 and 1073 K.

The infrared absorption of H_2O at 3465 and 1633cm−1 in Fig. 3decreased gradually for the six samples and almost disappeared for sample e. Combining DSC curves with infrared absorption for the six samples, it can be seen that the physically adsorbed water was removed

mainly at about 343K and the process was accompanied by an endothermic change. However, the physically adsorbed water could not be removed completely at 343K. Although the first peak of DSC for samples e and f disappeared, infrared absorption of H2O at 3465cm−1 for sample f could still be observed. A trace amount of t0he physically adsorbed water exists on the surface even if the silica was dehydrated at 1273K for hours. The diagram for their moving of the physically adsorbed water was shown in Fig. 4(I).In previous report, the water molecules can physically be adsorbed on the surface by formation of hydrogen bonds with three kinds of silanol groups (isolated free, geminal free and vicinal silanol] (Zhuravlev, et-al, 2000), (Tielens, et-al, 2008). Many other researchers have reported that geminal silanols amount to 9–30% and isolated silanlos amount to about 20% of the total Silanol population on amorphous silica .The second peak in Fig. 1(a) appeared at about 709K for samplesa–d. The chemisorptions water (Silanol groups) on the surface startsto condense and evolve water extensively, as shown in Fig. 4(II).The infrared absorption of bending vibration at 972 cm−1 (paired silanol groups) has disappeared (Fig. 2b and c), while the infrared absorption of stretching vibration at 812 cm−1 still exists for sample and f, the new infrared absorption (Si–O, 620cm−1) has justappeared. This phenomenon is attributed to the formation of Si–O on the surface because of the chemisorption water (silanol groups) was removed gradually. It can also be observed that the infrared absorption of stretching vibration still appear for sample f. These results suggest that the chemisorption water (silanol groups) beremoved mainly at 709 K, but they could not be dehydrated completely even at 1273K.

For the samples, another exothermic peak appears at about1210 K. Besides, the exothermic process was also observed for the samples e and f when the temperature is above 1100 K. It is obvious that all samples

were dehydrated above 1100 K. On one hand, the chemisorption water (silanol groups) on silica surface was dehydrating.

the surface of siloxane network start to condense and evolve water,as shown in Fig. 4(III). Deeper silanol groups are more stable, and can be removed only at higher temperature. The minima peaks inFig. 1(a) appeared at about 500K for samples e and f is attrbuted to alittle phase transition (β-cristobalite α-cristobalite), (Zhou,1999) . Thephase transition cannot be observed for other samples because the exothermal process in the temperature range has masked the minima peak.

According to Langmuir surface area of silica, the OH density and the physically adsorbed water can be calculated by the TG results.

Because the physically adsorbed water was lost mainly between323 and 473K, the mass loss in this range was thought as the weight of the physically adsorbed water on surface. Similarly, the mass loss in the range between 473 and 1073K was the weight ofthe chemisorption water (silanol groups) on surface. And the mass loss in the range between 1073 and 1273K was the weight of the"buried" silanol groups below the surface. The calculation equation is:

$$D = M/SW \times L$$

Where D is H_2O or OH density, M is mass loss per mg silica, S is Langmuir surface area of silica per mg (0.198m2/mg), W is molar weight of H_2O or OH, and L is Avogadro's constant.

For sample a, the physically adsorbed water and silanol groups on surface were 9.80 and 8.20nm−2, respectively. And the physically adsorbed water and silanol groups of the sample f were about 0nd 2.50nm−2, respectively. The results suggest that the physically adsorbed water be almost lost completely with heat treatment of 1273K for hours. Neither OH group on surface nor the "buried"silanol group (Sindrof and

Maciel, 1983) below the surface could be removed completely at this temperature (*Peng et al,2009).*
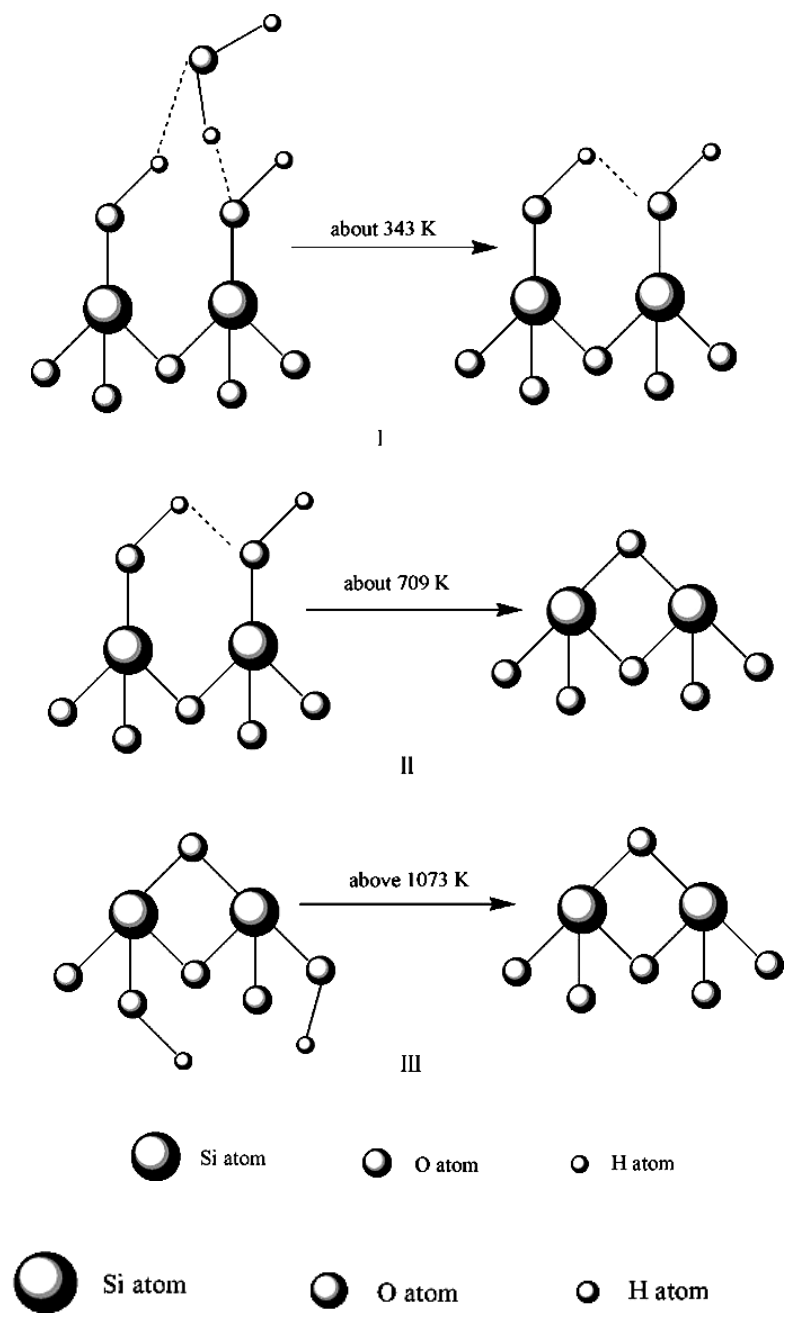
Fig1. 4. The schematic diagram of dehydration process at different temperature

On a surface that is fully hydroxylated, the H2Omolecules were adsorbed and covered all SiOH groups because of multiple hydrogen bonding.

As the temperature increases, the physically adsorbed water begins to be removed first, then silanol groups on surface is dehydrated, and finally silanol groups below the surface is dehydrated. This result is consistant with Zhuravlev's conclusion. He also reported the main three stagesof the dehydration, stage I (298–463 K): the physically adsorbed water; stage II (463–673 K): the silanol groups of the surface; stage III (673–1173 K): the internal silanol groups.

The silica surface produces siloxane bridges only when the sample was heated above 1273 K. Actually, the process also took place at the same time in a wide temperature range. For physically adsorbed water,there are different stable combination ($Si(OH)_4 \cdot H_2O$, $Si(OH)_4 \cdot 2H_2O$, $(OH)4 \cdot 3H2O$, and so on) with an increasing number of water molecules per silica unit, the trend in SiO–H bond elongation isemphasized, thus, the dehydration of the water must take place in several successive steps (Zhuravlev, et-al, 2000) . Since the silicon atoms on thesurface of amorphous silica are not in an exactly regular geometrical arrangement, the physically adsorbed water and OH groups on surface will not be exactly equidistant from each other. Therefore, they are not all equivalent either in their behavior or in adsorption, chemical reactions and thermodynamics. As to silanol groupsbelow the surface, in the process of polymerization of monomer to form particles, the OH groups of monosilicic acid might not be dehydrated because of rapid polymerization rate and the burial within the particles (Dubini, et-al, 1964).

1.9. Silicification in sorghum:

Sorghum belongs to a group of economically important, silicon accumulating plants. X-ray microanalysis coupled with environmental scanning electron microscopy (ESEM) of fresh root endodermal and leaf epidermal samples confirms histological and cultivar specificity of silicification. In sorghum roots, silicon is accumulated mostly in endodermal cells. Specialized silica aggregates are formed predominantly in a single row in the form of wall outgrowths on the inner tangential endodermal walls. The density of silica aggregates per square mm of inner tangential endodermal cell wall is around 2700 and there is no significant difference in the cultivars with different content of silicon in roots. In the leaf epidermis, silicon deposits were present in the outer walls of all cells, with the highest concentration in specialized idioblasts termed 'silica cells'. These cells are dumb-bell shaped in sorghum. In both the root endodermis and leaf epidermis, silicification was higher in a drought tolerant cultivar Gadambalia compared with drought sensitive cultivar Tabat. Silicon content per dry mass was higher in leaves than in roots in both cultivars. The values for cv. Gadambalia in roots and leaves are 3.5 and 4.1% Si, respectively, and for cv. Tabat 2.2 and 3.3%. However, based on X-ray microanalysis the amount of Si deposited in endodermal cell walls in drought tolerant cultivar (unlike the drought susceptible cultivar) is higher than that deposited in the leaf epidermis. The high root endodermal silicification might be related to a higher drought resistance (http://www.ncbi.nlm.nih.gov/pubmed/12010471, 24/9/2014 at 7:11 AM).

1.1 0. Silica in corn:

Ash and silica content and their depositional patterns in different tissues of the mature corn plant (*Zea mays* L.) were determined. Ash and silica were highest in the leaf blades (up to 16.6 and 10.9 per cent,

respectively) followed by the leaf sheath, tassel, roots, stem epidermis and pith, and ear husk. The percentage of ash as silica was also highest in the leaves. Silica was extremely low in the kernels. The upper stem epidermis and pith contained nearly twice the silica content as did the lower portion. The patterns of ash and silica distribution were similar in plants grown in two different areas of Kansas, but were in lower concentration in the leaves and leaf sheaths from the area with lower soluble silica in the soil. Silica was deposited in the epidermis in a continuous matrix with cell walls showing serrated interlocking margins in both leaves and stem. Rows of lobed phytoliths of denser silica were found in the epidermis as well as highly silicified guard cells and trichomes. The silica matrix of the epidermis appears smooth on the outer surface and porous or spongy on the inner surface (http://aob.oxfordjournals.org/content/45/5/549, 27/9/2014 at 11:27 PM).

1.1 1. Applications of silica:

Due to the variety in porous structure, particle size and surface area, pure silica gels and powders find a very wide range of applications. Variation in preparation methods and parameters allows the tailoring of the substrate properties for specific application Needs. The main features in the silica applications are its porosity, active surface, Hardness, particle size and the viscous and thixotropic properties. Although mostApplications are based on a combination of those, a classification according to the main Properties of interest may be set up (Vansant, et-al, 1968).

1. 11.A. Porosity:

Pure silica is used as a stationary phase in various types of liquid chromatography (Smith, 1988). 2 g In size exclusion chromatography(You, et-al, 1979) the separation of polymer compounds

is effectuated on basis of diffusion rate of variably-sized molecules through a micro porous silica packing with uniform pore size.

1.11. B Active surface:

The silica surface allows variable types of interactions in which the large specific Surface area as well as the surface site chemistry plays an important role. Both topics will be discussed in detail below. Concerning the applications, three types of Interactions may be discerned"

* adsorption" in liquid-liquid chromatography, silica packing's are used, which acts as a sponge to hold the static liquid phase as an active adsorbent. The pure silica may also be used as a stationary phase in column liquid chromatography. The adsorption Characteristics are also applied in the use of silica as a catalyst base. Active catalyst Species are adsorbed onto high-area silica. The adsorption of dye molecules on silica Powders in coatings, paintings and painting inks results in less intense and flatted color.

* Absorption: silica is used in various forms (from finely divided powders to small Granules) as a desiccant. This is probably the largest of all applications. Water is physically and chemically bound to the silica surface. Silica is added to any package Product, which may be subjected to corrosion or deterioration by moisture.

* Ion-exchange: the ion-exchange capacity of the silica surface is used for the Bounding of metal complexes and surface metal cat ions. This property is applicable in the chromatographic separation of cationic species.

The nature of the silica surface may be changed by modification with a variety of molecules, causing a still broader range of applications(Bannasch and Stam, 1964), (Markova and Vydra, 1966).

1.11. C. Hardness:

The hardness and abrasive properties of silica gels and powders are of interest in their

use as reinforcing agents in composite materials.

Wear resistance and tensile strength of rubbers and polymers are increased by the introduction of silica in the organic network. In order to preserve these improved qualities in wet conditions, however, the silica surface has to be modified to assure interfacial bonding (Pleuddemann, 1991).

1.11. D .Particle Size:

Due to their disperse character and small particle size, silicas are used as flow aids, I.e. they are used to improve the flow behavior of other materials. The adsorption of the fine silica particles on other type powdered compounds reduces inter-particle Inter actions. Particle adhesion, electrostatic adhesion, Van Der Waals forces and liquid bridge formation is reduced or avoided (Frech, et-al, 1993). This allows free-flowing behavior of strongly interacting or irregularly shaped powdered materials.

1.11.E.Viscosity and thixotropy:

When suspended colloidal particles form a network through the liquid, viscosity is increased. The thickening and thixotropic effects for silica gel are used in a large number of applications. The silica is mixed with paints, coatings, inks, pharmaceutical and cosmetics with this purpose (Fratzsceh, 1983).

1.11. F. Uses of Silica:

An estimated 95% of silicon dioxide produced is consumed in the construction industry, e.g. for the production of Portland cement. Other major applications are listed below.

(Wikipedia, 2014)

1.11. F.1. Precursor to glass and silicon metal:

Silica is used primarily in the production of glass for windows, drinking glasses, beverage bottles, and many other uses. The majority of optical fibers for telecommunication are also made from silica. It is a primary raw material for many ceramics such as earthenware, stoneware, and porcelain. It is used to produce elemental silicon. The process involves carbothermic reduction in an electric arc furnace.

$$SiO_2 + 2\,C \rightarrow Si + 2\,CO$$
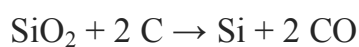
(Wikipedia, 2014)

1.11. F.2. Food and pharmaceutical applications:

Silica is a common additive in the production of foods, where it is used primarily as a flow agent in powdered foods, or to absorb water in hygroscopic applications. It is the primary component of diatomaceous earth. Colloidal silica is also used as a wine, beer, and juice agent. In pharmaceutical products, silica aids powder flow when tablets are formed.

(Wikipedia, 2014)

1.11.F.3. Other Uses:

A silica-based aerogel was used in the Stardust spacecraft to collect extraterrestrial particles. Silica is also used in the extraction of **DNA** and **RNA** due to its ability to bind to the nucleic acids under the presence of chaotropes. As hydrophobic silica it is used as a defoamer component. In hydrated form, it is used in toothpaste as a hard abrasive to remove tooth plaque.

In its capacity as a refractory, it is useful in fiber form as a high-temperature thermal protection fabric. In cosmetics, it is useful for its

light-diffusing properties and natural absorbency. It is also used as a thermal enhancement compound in ground source heat pump industry.

(Wikipedia, 2014)

1.11. G. Health effects of Silica:

Silica ingested orally is essentially nontoxic, with an **LD**50 of 5000 mg/kg. On the other hand, inhaling finely divided crystalline silica dust can lead to silicosis, bronchitis, or cancer, as the dust becomes lodged in the lungs and continuously irritates them, reducing lung capacities. Prior to new rules issued in 2013 **OSHA** allowed 100 micrograms a cubic meter of air. The new regulations reduce the amount to 50 $\mu g/m^3$ down from 100 $\mu g/m^3$. The exposure limit for the construction industry is also set at 50 $\mu g/m^3$ down from 250 $\mu g/m^3$.

In the body crystalline silica particles do not dissolve over clinically relevant periods. Silica crystals can activate some inside macrophages and dendritic cells and thereby result in processing of pro-Interleukin 1 beta into its mature form. Chronic exposure to silica may thereby account for some of its health hazards, as interleukin-1 is a highly pro-inflammatory cytokine in the immune system. This effect can create an occupational hazard for people working with sandblasting equipment, products that contain powdered crystalline silica and so on. Children, asthmatics of any age, allergy sufferers, and the elderly (all of whom have reduced lung capacity) can be affected in much less time. Amorphous silica, such as fumed silica is not associated with development of silicosis, but may cause irreversible lung damage in some cases. Laws restricting silica exposure *with respect to the silicosis hazard* specify that they are concerned only with silica that is both crystalline and dust-forming.

A study that followed subjects for 15 years found that higher levels of silica in water appeared to decrease the risk of dementia. The study found an association between an increase of 10 milligram-per-day of the intake of silica in drinking water with a decreased risk of dementia of 11%.Crystalline silica is used in hydraulic fracturing of formation which contain tight oil and shale gas, a use which presents a health hazard to workers. (Wikipedia, 2014)

Experimental

2.1 Materials and equipments:

2.1.1 Materials:

- Nitric acid (LOBAL chemie, 69.72 %).

- Sodium hydroxide (Nice, 96 %).

- Methyl red indicator (LOBAL chemie, 75%).

2.1.2 Equipments:

- Conical flasks (250 ml).
- Bakers (100ml, 250 ml, 500ml and 1).
- Volumetric flasks (250 ml and500 ml).
- Glass rods.
- Crucibles.
- Sensitive balance.
- Magnetic stirrer.
- Oven (110 ∘C).
- Furnace (700 ∘C).

2.2 Methods:

2.2.1 Sample preparation:

The samples were collected and sun dried for more than ten days. The dried samples were then crushed to sample sizes and washed with diluted Nitric acid (3M) for about four hours with constant stirring. They were then washed with copious amount of water several times followed by distilled water until the complete removal of nitric acid.

After washing process, the samples were dried in oven for about 3-4 hours at 110 °C, and then weighed. The samples were burned in the furnace for about 5hours at 700 °C and then weighed.

2.2.2 Extraction of silica:

Affixed amount from samples were weighted and according to these weight affixed amount from sodium hydroxide (1M) were added, then the solution of samples were put on magnetic stirring about (20-24 hours), in this step sodium silicate was formed. After that nitric acid (3M) was added gradually until sodium silicate was hydrolyzed and the gel was formed in PH_5, Then the gel was took for about (24 hours) to complete the precipitation process.

2.2.3 Characterization of Silica:

Fourier Transform Infra-Red spectroscopy:

Fourier Transform Infra-Red (FT-IR) spectroscopic analysis was conducted on FT-IR spectrometer (Shimadzu, model 8400). The FT-IR spectra of silica extracted from the ashes of sorghum husk (SiO_2), corn leaves (CL-SiO_2), corn cock (CC-SiO_2) and corn silk (CS-SiO_2) were obtained in the wave number range of 400-4000 cm^{-1}, with KBr discs. The KBr disk was prepared at weight ratio of KBr (spectral grade) to silica sample of about 20:1.

Results and Discussions

3.1 Preparation of silica:

The ash content and percentages of silica was extracted from these ashes are listed in Table 3.1. The percentages were found to be very high in the sorghum husk (8 %) and very low in the corn cock (1 %). Whereas, the yields of silica extracted from the ashes of all samples were found to be 63 %, 90 %, 90 % and 98 % for sorghum husk, corn silk, corn leaves and corn cock, respectively. It is very obvious that the yields of silica decreased with the increase in the ash content from the sample, this could be due to nature of samples or content of sample from silica.

Lenza(2001) used formamide in the preparation of silica and found in the presence of formamide, the Si-O-Si bonds are stronger and belong to a more cross-linked structure. The samples obtained in the presence of formamide have larger pore volume and its pore structure is in the range of mesoporosity.

Table 3.1: Yield weights and percentages of silica extracted from corn plant and sorghum bicolour

Samples	Weight before burn	Weight after burn	Ash %	Yield %
Sorghum husk	64.64 g	4.96 g	7.67 %	62.83 %
Corn silk	7.42 g	0.25 g	3.36 %	90.00 %
Corn leaves	10.57 g	0.16 g	1.54 %	90.00 %
Corn cock	16.03 g	0.12 g	0.75 %	98.00 %

3.2 Characterization of Silica:
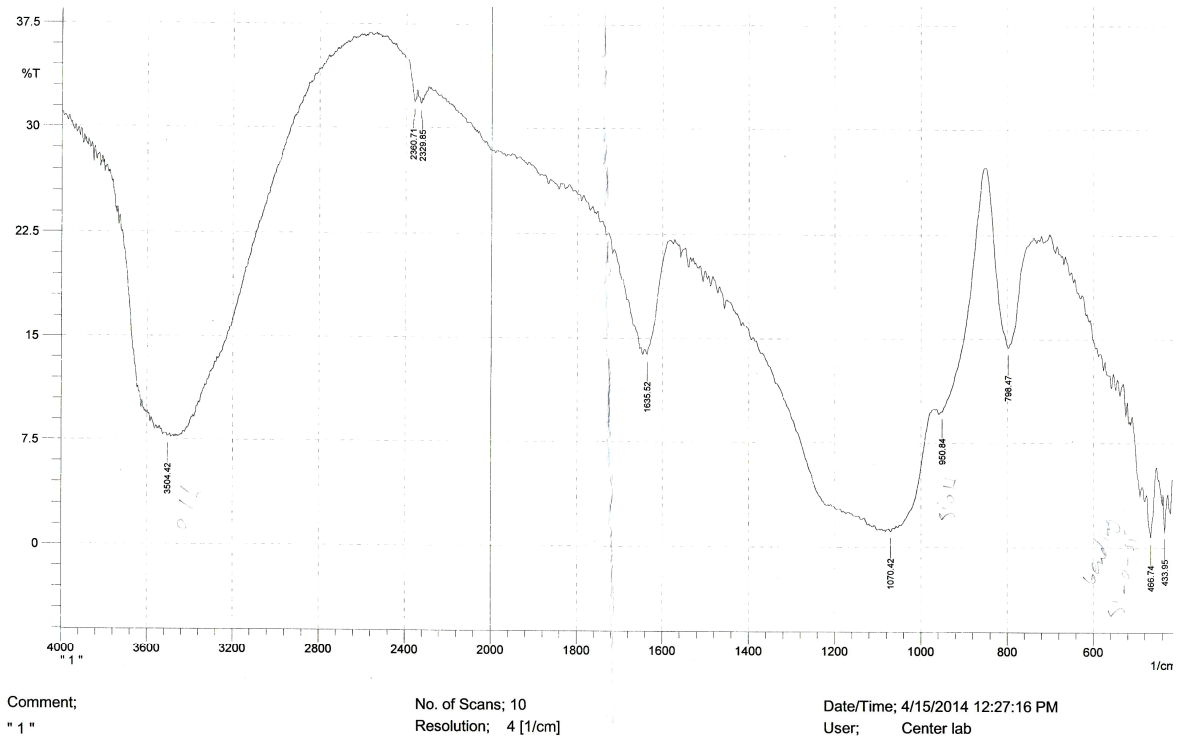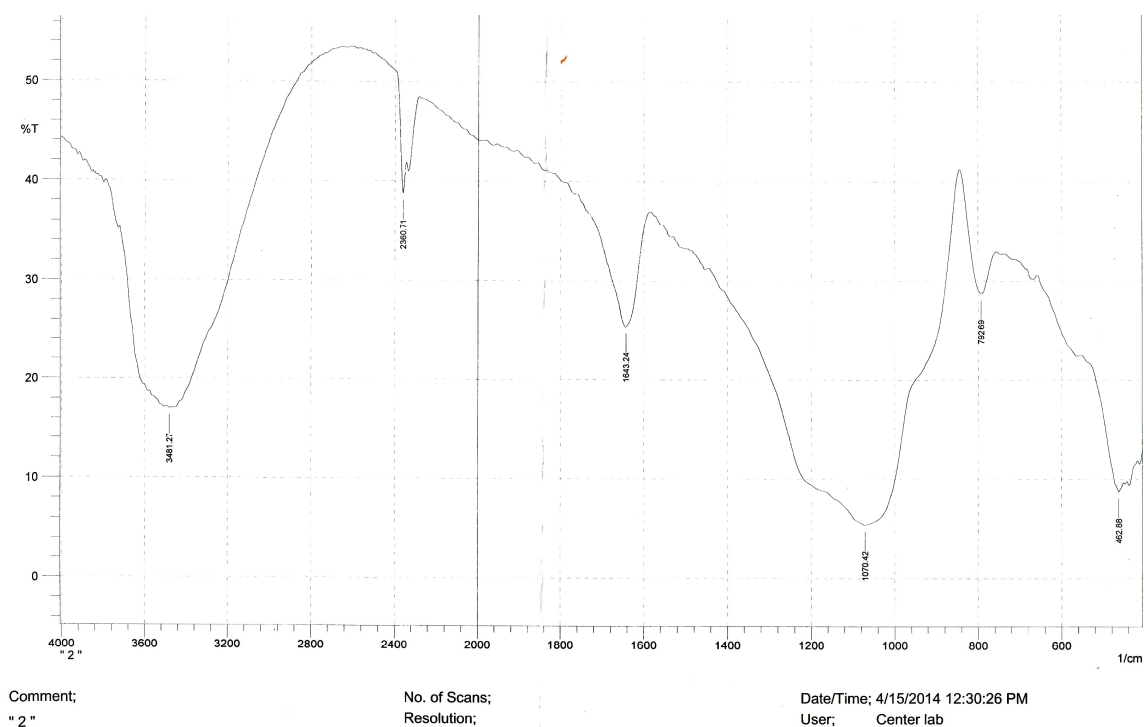

Figure 3.1 shows the silica spectra present several frequency regions in corn silk.

3.2.1 Corn Silk:

The extracted silica was characterized by FT-IR spectrometer and the results obtained are depicted in Figure 3.1. The signal at 3504.42 cm-1 is due to H_2O stretching vibration(Orcel, et-al, 1986), (Wood, et-al, 1983), (Almeida and Pantano, 1990), (MCDonald,1958), (Bartholomeu, et-al, 1980) and the band at 2360.71 cm-1 is due to atmospheric CO_2, whereas, the band at 1635.52 cm-1 is assigned to molecular water and the peak at 2329.85 cm-1 is due to CO_2 overtones (Orcel, et-al, 1986), (Bartholomeu, et-al, 1980), (Wood, et-al, 1983). the band at 1070 cm-1 is

due to asymmetric stretching vibrations of Si-O-Si. The signal at 798.47 cm-1 is due to symmetric stretching vibrations of Si-O-Si, and the band at 950.84 cm-1 is due to stretching vibration of free silanol groups on the surface of the amorphous silica solid whereas The bands at 466.74 cm-1 and 433.95 cm-1 are due to Si-O-Si bond vibrations (Brinker and Scherer, 1990), (Orcel, et-al, 1986), (Almeida and Pantano, 1990), (Schraml, et-al, 1992), (Chmel, et-al, 1990) (Parril, 1994), (Bertoluzza, et-al, 1982) .

Figer3.2 showed silica spectra percent several frequency regions in corn cock.

3.2.2 Corn cock:

The extracted silica was characterized by FT-IR spectrometer and the results obtained are depicted in figer3.2. The band at 3481.27 cm-1 is due to molecular hydrogen bonded to each other (Orcel, et-al, 1986),

(Wood, et-al, 1983), (Almedia and Pantano, 1990), (MCDonald,1958), (Bartholomeu, et-al, 1980) , whereas, the peak at 2360.71cm-1 is due to atmospheric CO 2and The band at 1643.24cm-1 is due to vibration of molecular water(Orcel, et-al, 1986), (Bartholomeu, et-al, 1980), (Wood, et-al, 1983) .the band at 1070.42 cm-1 is due to asymmetric stretching vibrations of Si-O-Si, whereas, The signal at 792.69 cm-1 is due to symmetric stretching vibration of Si-O-Si and band462.88cm-1 is due to Si-O-Si bond bending vibration (Brinker and Scherer, 1990), (Orcel, et-al, 1986), (Almeida and Pantano, 1990), (Schraml, et-al, 1992), (Chmel, et-al, 1990) (Parril, 1994), (Bertoluzza, et-al, 1982) .
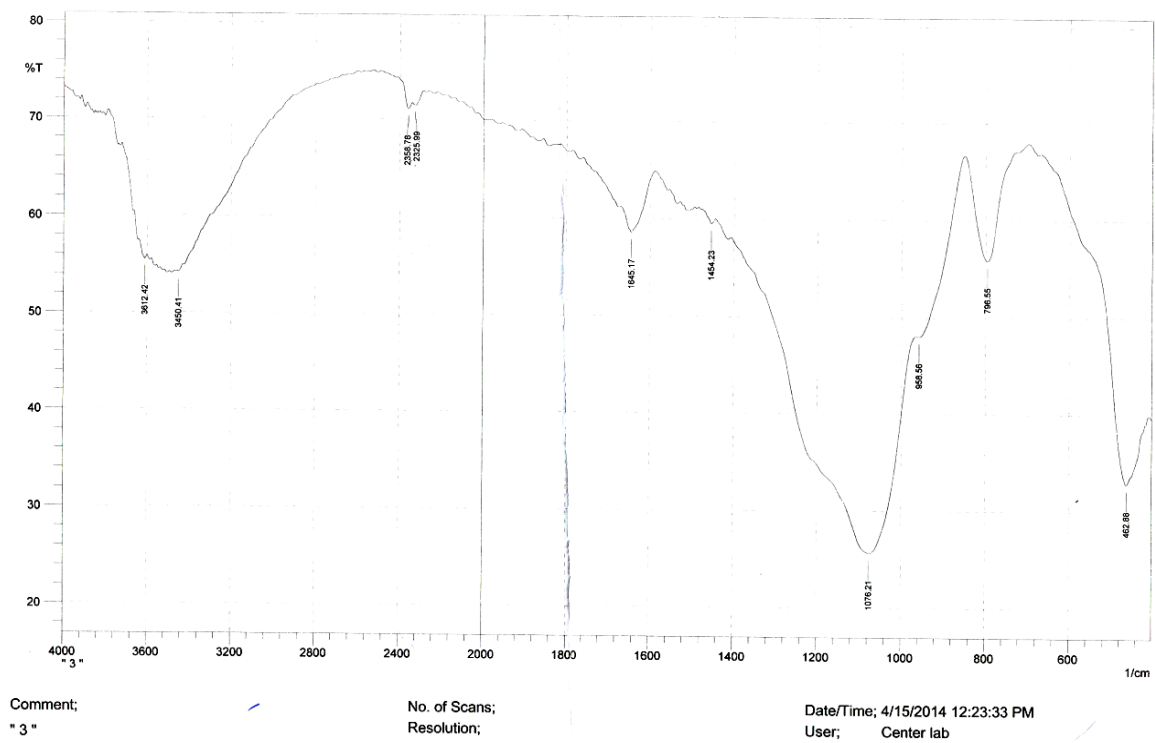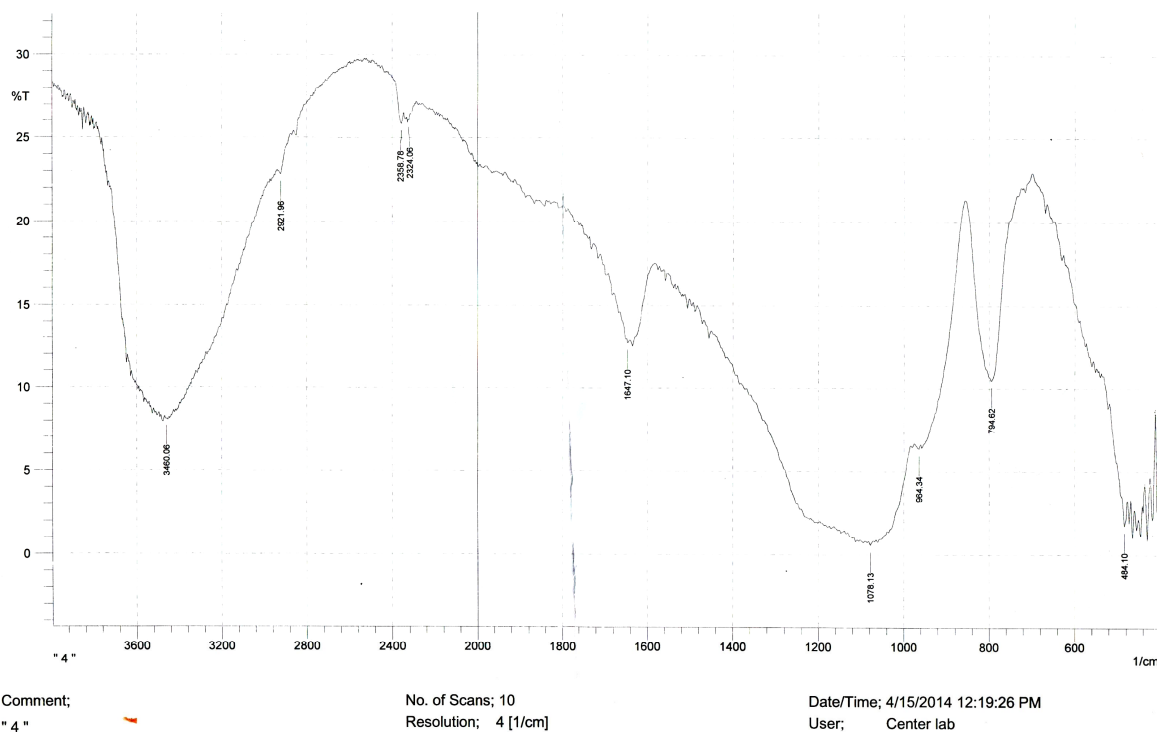

Figer3.3 showed silica spectra percent several frequency regions in corn leaves.

3.2.3Corn leaves:

The extracted silica was characterized by FT-IR spectrometer and the results obtained are depicted in figer3.3. The signal at 3612.42 cm-1 is due to the stretching vibration of H_2O, whereas, the band at 3450.41cm-1 is due to molecular water hydrogen bonded to each other (Orcel, et-al, 1986), (Wood, et-al, 1983), (Almedia and Pantano, 1990), (MCDonald,1958), (Bartholomeu, et-al, 1980). The peaks 2358.7cm-1 and 2325.99 cm-1 are due to atmospheric CO_2, and the band 1645.17cm-1 is due to vibrations of molecular water, whereas, The signal at 1454.23cm-1 is due to vibrations of CH bonds (Orcel, et-al, 1986), (Bartholomeu, et-al, 1980), (Wood, et-al, 1983). The band at 1076.71 cm-1 is due to symmetric stretching vibrations of Si-O-Si bond and The band at 958.56 cm-1 is due to stretching vibration of free silanol groups on the surface of amorphous silica , whereas, the band at 796.55cm-1 is due to symmetric stretching vibrations of Si-O-Si bonds and the band at 462.88cm-1 is due to Si-O-Si bond bending vibration (Brinker and Scherer, 1990), (Orcel, et-al, 1986), (Almeida and Pantano, 1990), (Schraml, et-al, 1992), (Chmel, et-al, 1990) (Parril, 1994), (Bertoluzza, et-al, 1982) .

Figer3.4 showed silica spectra present several frequency regions in sorghum husk.

3.2.4 Sorghum husk:

The extracted silica was characterized by FT-IR spectrometer and the results obtained are depicted in figer3.4. The band at 3460.06 cm-1 is due to H_2O stretching vibrations(Orcel,1986), (Wood, et-al, 1983), (Almedia and Pantano, 1990), (MCDonald,1958), (Bartholomeu, et-al 1980) , and the peak at 2921.96 cm-1 is due to a symmetric fundamental stretching vibrations of CH2 and CH3, whereas, the bands 2358.78cm-1 and 2324.06cm-1 are due to atmospheric, whereas, the signal at 1647.10 cm-1 is due to vibrations of molecular water (Orcel, et-al, 1986), (Bartholomeu, et-al 1980), (Wood, et-al, 1983) . The signal at 1078.13 cm-1 is due to symmetric stretching vibrations of Si-O-Si bond and the band at 964.34 cm-1 is due to stretching vibration of free silanol groups on the surface of the amorphous silica solid, whereas the band at 794.62

cm-1 is due to symmetric stretching vibrations of Si-O-Si bonds and the band at 484.10 cm-1 is due to Si-O-Si bond bending vibration (Brinker and Scherer, 1990), (Orcel, et-al, 1986), (Almeida and Pantano, 1990), (Schraml, et-al, 1992), (Chmel, et-al, 1990) (Parril, 1994), (Bertoluzza, et-al, 1982).

Conclusion and recommendations

4.1 Conclusion:

Silica was extracted from sorghum husk, corn leaves, corn silk and corn cock through the calcination of the plant species then dissolution in 1M solution of sodium hydroxide. The silica was formed from the alkaline solution by a titration against 3M nitric acid using a sol-gel method. The percentage yield of all samples were calculated and were found to be 63%, 90%, 90% and 98% respectively. The silica samples were characterized by FT-IR spectroscopic analysis and were found to contain all the characteristic peaks of amorphous silica.

4.2 Recommendations

In this project, the silica was extracted successfully through simple methods, but further research works are likely needed hence we recommend the following points:

- Study the presence of silica in a corn planted at different climatic conditions, seasons and soils.
- Study the effect of different mineral acids in the gelation process.
- Study the use of different alkalis, such as KOH and LiOH, for the extraction of silica from the ash.
- Study the presence of silica in various sorghum species.

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