

# Green Synthesis of Silicon Dioxide from Eleusine Indica and Its Characterisation

Sabira Bi M. A. Shaikh, Anurag Naik

Parvatibai Chowgule College of Arts and Science Automous  
Margao – Goa

**Abstract** - *Eleusine indica* L. commonly known as the Indian goosegrass, wire grass or crowfoot grass belonging to Poaceae or Gramineae family was scrutinized in this study. The leaf blades were studied to observe the appearance of Phytolith structures which are microscopic silica bodies produced by many grasses which aids in their physical support. The extraction of silica was accomplished by acid treatment of these leaves in two cycles for 16 hours at 80°C each cycle. The oxidation process of synthesized silica was carried out using Hydrogen peroxide for 16 hours at 80°C to produce silicon dioxide (SiO<sub>2</sub>). The characterization studies were processed using X-ray diffraction, scanning electron microscope and energy dispersive X-ray (SEM – EDX), Raman spectrometer, Fourier Transform Infra-red spectroscopy (FT-IR). The obtained results were interpreted and compared with the standard. The comparative observations were reported.

**Keywords** - *Eleusine indica*, Poaceae, Phytoliths, Biogenic silica, Silicon dioxide (SiO<sub>2</sub>).

## I. INTRODUCTION

### Chemistry of Silica

Silica is the common name for the chemical compound, Silicon dioxide (SiO<sub>2</sub>). This binary compound is made up of one silicon atom bonded to two oxygen atoms and represented by the chemical formula SiO<sub>2</sub>. Silicon (SiO<sub>2</sub>) being second most abundant element on the Earth's crust found as quartz or sand after oxygen, it has become the focal point of many researchers to work on. It makes up 59% of the mass of Earth's crust and is the main component that comprises more than 95% of known rocks. It also transpires in nature, that is in soil, sand, rocks, plants and in agricultural waste as crystalline, polycrystalline or amorphous silicon (SiO<sub>2</sub>).

### Classification of Silica

Silicon dioxide encircles its miscellaneous forms depending on four main features: Surface composition, crystal structure, porosity and dispersity. (L.T. Zhuravlev, 2009)

### Surface composition:

Masses of silica derivatives contain organofunctional groups chemically bonded at the surface that are formed by means of surface reactions. They can be

distinguished based on the type of bond by which the functional groups are attached to the surface atoms of silicon. (L.T. Zhuravlev, 2009)

### Crystal structure:

On the basis of bulk structure of silica, it is defined as amorphous silica and crystalline silica. Amorphous silica is porous and has limited information on its structure. Hence, non-porous crystalline silica has become well known to be used as reference at most of the instances. Unlike crystalline forms, porous silica is kinetically and thermodynamically unstable. In several reactions it can reify more stable, low-energy state. Therefore, in thermal processes in which porous silica is involved, non-porous crystalline silica is the final product. (L.T. Zhuravlev, 2009)

### Porosity:

This implies a solid silica with a pore system that can be characterized by width of the pores, their distribution and shapes within the solid particle. High porosity leads to high surface area. Porous silica are amorphous. It is noticeable that, congregation of smooth discrete silica particles is not regarded as porous silica. Also, high surface area is observed in dispersed silica system due to their high dispersity but they are contemplated as non-

porous. Pore system can be regarded as dispersed system. Aerogel and colloidal silica are obtained when the porous particles smaller than 1  $\mu\text{m}$  are distributed in a dispersion medium. (L.T. Zhuravlev, 2009)

#### **Dispersity:**

Considering dispersity, silica is available as aerogels, hydrogels, xerogels, soluble silica and silica sols. These are dispersed systems known as amorphous silica where solid is distributed in gaseous or liquid dispersion medium. (L.T. Zhuravlev, 2009)

#### **Properties of Silica**

##### **Chemical transformations (Reactions):**

At customary temperatures, silica is chemically unsusceptible to numerous habitual reagents. Regardless of how, it undergoes broad heterogeneity of chemical transformation under conditions such as elevated temperature, in the presence of aluminium and aluminium halides, silica can be converted to silane in high yields by reaction with hydrogen. Silicon itself is not hydrogenated under these conditions. Depending on the forms, sample and pretreatment, reactivity can be confirmed. In number of set of conditions, finely divided amorphous silica is considerably more reactive than bulk crystalline silica. At 1300 - 1400°C, silica is reduced using hydrogen, Carbon and variety of metallic elements. At 200-250°C, reduction with sodium and lithium takes place with the formation of silicate and metal oxide. Calcium, aluminium and magnesium can also reduce silica at 800-900°C. Excluding these, other metals known to employ in reduction of silica to the element includes cerium, niobium, iron, neodymium, lanthanum, manganese and uranium. Large number of basic oxides forms silicate indicating the acidic character of silica. Compounds including Si-C and Si-O-C are resulted from the reaction of silica with organometallic and organic compounds. (Robert E. Patterson, 2000)

##### **Solubility:**

Considering solubility of silica, there is geological significance in interaction of varied forms of silica with water. This is applicable steam power engineering where its deposition on turbine blades and volatilization of silica may occur, also in

hydrothermal processes for production of synthetic quartz crystals and in producing commercially significant colloidal silica, soluble silicate and silica gel.

Reported values for solubility of quartz at room temperature as  $\text{SiO}_2$  are in the range of 6-11ppm. Quintessential values for colossal amorphous silica are 70 ppm, for other amorphous silica's 100-130ppm. Solubility is directly proportional to temperature, so increasing solubility with increasing temperature at about 200°C is reported. Solubility comes into view to be minimum at about pH 7 and increases noticeably above pH 9. At higher temperature the solubilities of modified crystalline silica are in the following order that parallels to the chemical reactivity : Trydymite > cristobalite > quartz. (Robert E. Patterson, 2000)

##### **Production of Silica**

Many processes can be availed for producing silica nano particles, including sol-gel method, hydrothermal processes, microwave processes and combustion synthesis. To produce silica on a wide range, most methods had been employed that entails the utilization of very high temperature processes, which are not only energy insensitive but also may be perilous to the environment due to voluminous generation of  $\text{CO}_2$  gas. In general, it can be asserted that a boundless preponderance of methods that produce silica are long-drawn-out and energy-intensive, produce silica with weak-matches and are incompetent, thus requiring low energy consumption, low  $\text{CO}_2$  generation and a legitimate method of silica production which cannot be overemphasized. (Firdaus, M., 2015)

##### **Occurance of Silica in plants**

Plants draw up silica from soil water as silicic acid and it is carried to different parts of the plant through vascular system. In plant cells, silica is present intracellularly as well as intercellularly. cytoplasm and vacuoles composed of intracellular silica whereas intercellularly, phytoliths are deposited in almost all parts of the plant i.e. in leaves, stem, roots, inflorescence, etc. In conjunction with silica, some of the plants also possesses nonsiliceous phytoliths embodied of magnesium oxalate, strontium oxalate,

strontium sulphate, Barium sulphate, calcium carbonate, calcium oxalate, calcium phosphate and calcium sulphate. (Muhammad Amjad Nawaz, 2019).

### Applications of Silica

One of the engrossing facts about silica-based NPs is that they provide a propulsion system for biomedical applications, and it is further riveting to note that silicon is biocompatible and bioactive. Silica has a melting point of 1,710°C and is chemically reactive with few compounds. Reaction of silica with hydrochloric acid is employed in industries in making semiconductors. Moreover, silica reacts with metal oxides such as lead oxide for producing laboratory-grade glassware.

Silica in liquid form demonstrates negative temperature expansion and as quartz, it possesses piezoelectric effect.

Silica can be availed as food additive as it is non-toxic. However silica is hazardous in finely-grained crystalline forms. If tiny crystals of silica are inhaled, they can damage and irritate the lungs and airways. This can result in something called silicosis, bronchitis and even lung cancer. (Robert E. Patterson, 2000)

Silicon dioxide coating is commonly employed as an insulator to reduce solar cell potential-induced deterioration when the PV module is installed outside. When exposed to light, the silicon dioxide layer absorbs energy and turns photons into free electrons, which can then be used to generate electricity. (A.S. Arul Prishya, 2023)

## II. LITERATURE REVIEW

### Silica in Plants: Biological, Biochemical and Chemical studies.

#### Heather A. Currie and Carole C. Perry

This paper justifies the evidence of presence of silica in plant cells which ranges from 0.1 to 10% (=103 - 105 mg Kg<sup>-1</sup>) based on its dry weight. It is present as Silicic acid, (Si(OH)<sub>4</sub>), correctly known as orthosilicic acid which is a rudimentary building block of silica and itself is a simplest silica. This is the result of its uptake by plants from the soil in its soluble form

(Si(OH)<sub>4</sub>). Therefore, in plants, silica exists as amorphous, hydrated and polymerized component caused by (Si(OH)<sub>4</sub>). The capability of uptake of silica by plants is considerably dissimilar between species. According to the research, Poaceae, Equisetaceae and Cyperaceae show high silica accumulation. Plants impoverished of silica are structurally feeble, susceptible to abnormal growth, reproduction and development.

A simple method for the production of pure crystalline silica from lemon grass.

M. Y. Nur Firdaus, H. Osman, H. S. C. Metselaar and A. R. Rozyanty.

Grasses are the major source of silica. The presence of silica in perennial grasses depend on the quantity of silicic acid in water absorbed by the roots. Furthermore, silica is higher in quantity in inflorescences, leaf sheaths, leaves then in the stem of the grasses. Silica from grasses is obtained by exposing it to elevated temperatures to remove carbon and other volatile components. Silica extraction techniques includes acid leaching and gasification. Acids like H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HCl is used which extracts several metals and enhances the specific surface area of the grass ash. This treatment on lemon grass yields high purity silica.

Effect of acid treatment on extraction of silica from cogon grass by using C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> and HCl acid.

#### N A Zarib, S A Abdullah and N A Jusri.

The focus of this paper is to study the effect of acid treatment on silica extraction from cogon grass. Acids used in this study to perform extraction of silica are citric acid and HCl. The results of characterisation studies from XRD, SEM, TGA indicates that the acid leaching treatment using 1.0 M HCl yields highest percentage of silica of amorphous structure while acid leaching using 1.0M citric acid produced silica with small porous surface. TGA analysis justifies the difference between the two leaching treatments. Accordingly, HCl is used in acid leaching treatment due to its strong acidity leading to more silica extraction compared to citric acid.

### **Silicon; the long forgotten element of plants.**

**Jean – Georges Barth**

Based on the recent physiological studies, silica has positive effects on plants development and growth. SiO<sub>2</sub> depositions are observed on the peripheral plant cells. These SiO<sub>2</sub> deposition increases with plants age as opposed to a decrease in tissues when aging. With regards to physiological tasks, SiO<sub>2</sub> can take over the function of lignins or cellulose in the plant by replacing carbon. It also causes enhancement of photosynthesis and development in plants by promoting light effects. Silica balances nutrient conditions in soil and leads to the reduction of biotic and abiotic stress on the plant.

### **Adsorption of heavy metals on silica-supported hydrophilic carbonaceous nanoparticles (SHNPs).**

**F. Di Natale, V. Gargiulo, M. Alfe**

This paper results probing conclusions on obliterating of Pb(II), Cd(II) and Ni(II) ions using hydrophilic carbon nanoparticles (HNPs) supported on silica beads to enhance their separation from treated water. These HNPs exhibit high obliteration efficiencies. The maximum adsorption capacity of SHNPs at a reference concentration of 0.2mM is 0.027 mmol g<sup>-1</sup>, 0.042 mmol g<sup>-1</sup> and 0.055mmol g<sup>-1</sup> for Pb(II), Cd(II) and Ni(II) ions respectively. On modelling analysis of adsorption isotherm, it is revealed that the Gibb's free energy of interactions between Pb(II) and Ni(II) ions is greater than that of Cd(II) ions indicating that the sorbents are more affine to intermediate acids as Pb(II) and Ni(II) ions than to soft acids as Cd(II) ions.

Removal of toxic heavy metals from river water samples using a porous silica surface modified with a new Beta-ketoenolic host.

Said Tighadouini, Smaail Radi, Abderrahman Elidrissi, Khadija Haboubi, Maryse Bacquet, Stephanie Degoutin, Mustapha Zaghrioui and Yann Garcia.

An up to the minute hybrid adsorbent material prepared by the immobilization of new conjugated Beta-ketoenol-pyridine-furan ligand onto silica matrix for the efficient removal of heavy metals from natural real water. The thermodynamical studies including adsorption isotherms, pH, selectivity, competitive adsorption, regeneration were

understood well to investigate the effect of ketoenol- pyridine-furan silica on the removal of Cd(II), Pb(II), Zn(II) and Cu(II) from aqueous solutions. The maximum sorption capacities for Cd(II), Pb(II), Zn(II) and Cu(II) were 48.30mg g<sup>-1</sup>, 47.07mg g<sup>-1</sup>, 96.17mg g<sup>-1</sup> and 32.15mg g<sup>-1</sup> respectively. Moreover, the material proved to be very stable. Its adsorption capacity remained greater than 98% even after five cycles of adsorption.

### **Synthesizing nano silica nanoparticles from Barley Grain waste: Effect of temperature on mechanical properties.**

Akhayere, Doga Kavaz, Ashok, Vaseashta.

Barley grass waste is known as an environmental burden. This paper reports the synthesis of nano silica(NS) nanoparticles from barley grass waste. This investigation involved application of temperatures of 400°C, 500°C, 600°C and 700°C to study its effects on the mechanical properties of the NS nanoparticles for the use of eco-friendly applications. The NS nanoparticles resulting from high temperature synthesis were characterized using X-ray diffraction (XRD), X-ray fluorescence(XRF) scanning electron microscopy(SEM), Fourier transform infrared(FTIR), energy-dispersive X- ray(EDX) analysis and Brunauer-Emmett-Teller(BET) analysis. Different characterization studies revealed the presence of Si, C and O in the synthesized nanoparticles.

### **Production of High Purity Amorphous Silica from Rice Husk**

Rohani Abu Bakar, Rosiyah Yahya, Seng Neon Gan.

This paper focuses on synthesizing Silica by controlled combustion of rice husk. Prior to combustion, acid leaching of rice husk is carried out using hydrochloric acid and sulphuric acid to obtain purer silica. It was noted that pre-treatment of rice husk with sulfuric acid enabled the hydrolysis and decomposition of organic components as revealed by thermogravimetry(TG) and SEM analysis. For systematic study, the combustion of un-leached, hydrochloric acid-leached and sulphuric acid-leached rice husks were performed in a muffle furnace at temperatures of 500°C, 600°C, 700°C, 800°C and 900°C for 2 hours. These resulted that all the samples produced amorphous SiO<sub>2</sub> with the average particle size range of 0.50 – 0.70 micrometer.

Effect of combustion on production of silica, particularly above 600°C was very small. Fluorescence (XRF) analysis was carried out for characterization studies. BET surface area of produced silica using hydrochloric acid was higher (218m<sup>2</sup>/g) than with sulfuric acid (209m<sup>2</sup>/g). The synthesized silica has potential as filler in plastics and rubber compounding.

#### **Characterization of bio-silica synthesized from cogon grass (*Imperata cylindrica*).**

**Kien-Who Kow, Rozita Yusoff, A.R. Abdul Aziz, E.C. Abdullah**

There are numerous applications of amorphous silica due to its pozzolanic properties and high surface area. This paper presents the synthesis of amorphous silica from cogon grass (*Imperata cylindrica*) by carrying out combustion at 650°C. By fitting thermogravimetric analysis (TGA) data to the Flynn-Wall-Ozawa model, kinetic parameters of combustion were determined. According to energy-dispersive X-ray (EDX) analysis, cogon grass has a relatively low silica content that is of about 2.9 wt%. Additionally, X-ray diffraction (XRD) revealed the amorphicity and purity of silica obtained and also that they are notably affected by the potassium content in the weed. Nevertheless, the impurities are removed by acid leaching process and the purity of silica is increased from 31.4 wt% to 83.4 wt%. By small-angle X-ray scattering (SAXS) analysis, it was determined that the primary particle size (a) and mass fractal dimension (D) of silica were 19.8nm and 2.4nm respectively.

Investigation of heavy metal ions adsorption behaviour of silica-supported Schiff-base ligands. Mahdieh Koorepazan Moftakar, Zohreh Dousti, Mohammad Reza Yaftian & Massomeh Ghorbanloo (2016).

This investigation reports that, for adsorption of heavy metal ions Cu(II) and Pb(II), modified Schiff-base silica particles have been selective and efficient adsorbents which were able to be used for multitudinous adsorption – desorption processes. This potential was scrutinized as a function of different parameters affecting the adsorption processes. It was revealed by anatomization of temperature dependency of the process that the

process of adsorption of ions is controlled by positive entropy changes. Various models including Temkin, Langmuir, Dubinin-Radushkevich and Freundlich isotherms, the adsorption process isotherm was investigated. The description of kinetics data was presented by pseudo-second-order model that allowed recommending a chemisorptions mechanism for the adsorption process.

#### **Silicon as a nutrient element for *Equisetum arvense*.**

**Ching – Hong Chen and Joyce Lewin**

This paper focuses on the presence of silicon concentrates as a nutrient element in young vegetative plants of *Equisetum arvense* L. For this study to be carried out, few plants of *Equisetum arvense* L. were collected and washed them with distilled water and were grown in several plastic bottles in a defined nutrient solutions with varying silica concentrates. Thereafter as measured by dry weight, there was increased growth with increasing silicon in the nutrient solution. Those plants with requisite Si supply materialize customary, healthy and in the kilter than those which were grown without added silica. In silica – deficient soots, deficiency symptoms such as wilting or drooping of branches, necrosis of the branch tips were observed. From this, the inference was drawn that Silicon is the vital element for healthy growth of *Equisetum arvense*.

#### **Highly Pure Silica Nanoparticles with High Adsorption Capacity Obtained from Sugarcane Waste Ash.**

Suzimara Rovani, Jonnatan J. Santos, Paola Corio and Denise A. Fungaro.

The focal point of this paper is synthesis of silica from Sugarcane waste ash. It is said that, in general run of things, silica nanoparticles obtained from green resources have number of applications in different materials such as adsorbents, membranes for fuel cells, catalysts, paints, Li-ion batteries and so on. According to the records, Brazil is the world's substantial producer of sugarcane and brings into being largest amount of sugarcane waste ash (SWA) which is a Si-rich source. This study probe a method for synthesizing highly pure SiO<sub>2</sub> NPs from SWA.

After completion of synthesis, NPs were characterized using inductively coupled plasma optical emission spectroscopy, X-ray diffraction, UV and FTIR spectroscopy, scanning and transmission electron microscopy (TEM), specific surface area and pore distribution and thermogravimetry analysis and applied as an adsorbent in the removal of acid orange 8 (AO8) dye from aqueous solution. The SiO<sub>2</sub> content was 88.68 and 99.08 wt% for SWA and SiO<sub>2</sub>NPs, respectively. TEM images presented the size range of SiO<sub>2</sub>nPs ranging from several micrometers to less than 20nm. The NPs showed a specific surface area of 131m<sup>2</sup>g<sup>-1</sup> and adsorption capacity of around 230 mg g<sup>-1</sup> for acid orange 8 dye. Moreover, after AO8 adsorption, recycling of SiO<sub>2</sub>NPs was very much competent with reuse for up to five cycles being possible. The conclusion reported that it was possible to obtain highly pure silica in a nanosize from the waste ash and produce an adsorbent with high adsorption capacity and reusability.

#### **Synthesis and characterization of silica nanoparticles prepared by Low – temperature Vapor – phase hydrolysis of SiCl<sub>4</sub>.**

**Feng Yan, Jianguo Jiang, Xuejing Chen, Sicong Tian and Kaimin Li**

This paper reports an economical and environmentally benign method for production of Silica nanoparticles by hydrolysis of silicon tetrachloride vapour with water vapour at a low temperature (150°C). For characterization studies, X-ray diffraction, X-ray fluorescence and scanning electron microscopy, size distribution analysis were employed. Pore diameter revealed that dry processing was suitable than wet processing for collection of nanoparticles. The porous amorphous silica had large specific surface area and high purity. It was prepared at a reaction temperature of 150°C. with reaction time of 5 seconds. Calcination at temperatures less than 600°C, verified the thermal stability of silica nanoparticles. By achieving hydrophobic modifications, it could remove surface hydroxyl groups while maintaining particle mesostructure. It was concluded that this method was inexpensivewith low reaction temperature having wide use in high-end applications.

#### **Synthesis of silica powders by pressured carbonation.**

**X. Cai, R.Y. Hong, L. S. Wang, X.Y. Wang, H.Z. Li, Y. Zheng, D. G. Wei.**

This paper reported the method for preparation of silica powders from inexpensive material of carbon dioxide (CO<sub>2</sub>) and sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>) by pressured carbonation in which carbon dioxide acts as a precipitating reagent. The precipitated silica was subjected to dynamic light scattering and transmission electron microscopy for size analyses and identification of microstructures. The size distribution, average particle size and yield of silica powders were affected by temperature, reaction time and concentrations of surfactants and sodium silicate solutions. It was observed that with concentration of sodium silicate and reaction temperature, the particle size of silica is increased and hence the yield of silica powders was increased with increased reaction time. The exclusive preparation conditions were experimentally determined for obtaining silica powders of nanosize, spherical shape, narrow size distribution and high purity unaccompanied by surfactant and sodium carbonate.

#### **Preparation of submicron spherical particles of silica by yhe water-in-oil microemulsion method.**

**Wei Wang, Xiao-an Fu, Ji-an Tang, Long Jiang**

This paper focuses on preparation of submicron spherical particles of colloidal silica by hydrolysis of sodium silicate in a Triton X-100-hexanol-cyclohexane-water microemulsion system. The obtained silica had an average particle diameter of about 30nm. Cyclohexane solution of Triton X-100 was used to describe the formation of a microemulsion. The investigation process for temperature effect and concentration of the aqueous Na<sub>2</sub>SiO<sub>3</sub> solution on solubilisation and results reported that solubilisation decreases with increased concentration of Na<sub>2</sub>SiO<sub>3</sub> and that an optimum temperature existed for the system.

#### **Silica deposition in Abaxial Epidermis before the Opening of Leaf Blades of Pleioblastus chino (Poaceae, Bambusoideae).**

**H. Motomura, T. Fujii and M. Suzuki.**

This paper justifies the presence of silica on leaf blades of *Pleiblastus chinoo* Poaceae family silica. Deposition process is one of the significant characteristics of Poaceae family. The deposition process, distribution and physiology of silica in this family have been utterly scrutinized. Among members of Poaceae family, Bamboo leaves with a fairly long life span, continuously amass silica in their tissues throughout their life. This process continues during the course of leaf opening and as well as after the leaf opening. It has been noted that depending on the cell types comprising the tissues, silica deposition process in relation to the ageing of the bamboo leaf after opening is differentiable. Through these studies, the clarification is reported about the silica deposition process in a developmental stage of the bamboo leaf. Distribution of silica was observed in the abaxial epidermis before the opening of the leaf blades of *Pleiblastus chino*.

#### **Preparation of Highly Monodispersed Hybrid Silica Spheres using a One-Step Sol-Gel Reaction in Aqueous Solution.**

**Yong-Geun Lee, Jae-Hyung Park, Chul Oh, Seong-Geun Oh and Young Chai Kim.**

This paper proposed a one-step preparation method of monodispersed hybrid silica particles which was studied using aqueous solution of organosilane chemicals. Usually, almost all of the hybrid silica materials were made by a complex method wherein the surface of silica substrate were coated with organic materials via chemical reaction. Nonetheless, there is novel technique that can be applied to synthesize colloidal hybrid particles without using substrate material. This method is simple, efficient and effective to control particle size of the product by changing experimental conditions.

Circumstantial characterization studies of this hybrid particles were carried out using thermogravimetric analysis (TGA), scanning and transmission electron microscopy (SEM) and (TEM) and were able to elucidate the properties and morphologies of silica particles.

#### **High-purification of amorphous silica originated from rice husks by combination of polysaccharide hydrolysis and metallic impurities removal.**

#### **Junko Umeda, Katsuyoshi Kondoh**

As per studies, rice husks and straw contains 70 – 75% organics and 15 – 20 mass% amorphous silica ( $\text{SiO}_2$ ) as non-eatable biomasses. After using the organic elements as fuels, the remnants contain large amount of silica that can be employed for its use in industrial materials when their purity is 99% mass or even greater. Consequently, in using rice husks and straws, one can reuse the high-purity silica which will aid in reducing the total cost of biomass. It is possible to acquire this high-purity silica from the remains left after air combustion of rice husks. High-purity amorphous silica with 99.5%-99.77% were synthesized from rice husks.

### **III. METHODOLOGY**

Green Synthesis of  $\text{SiO}_2$  from *Eleusine indica* and Its Characterisation

#### ***Eleusine indica* – a source of Silica**

The Poaceae family consisting of several species of grass has one of such rapidly growing diverse weed named as *Eleusine indica* whose inflorescence is composed of 2-13 flattened, shiny, finger – like spikes that emerge from a common point and each spike is divided into two rows of sessile spikelets.



**Figure 1.0-*Eleusine indica* L.**

Source :

<https://stock.adobe.com/in/images/indian-goosegrass/344843330>



Figure 2.0-Eleusine indica L. inflorescence

Leaf of Eleusine indica may lie flat or be folded. The base of the leaf which wraps around the stem is smooth.



Figure 3.0-Eleusine indica L leaves.

Source : <https://images.app.goo.gl/H5jTEd7Xe8zqfdR28>

The leaf blade of Eleusine indica was observed under microscope to confirm the presence of Phytoliths which are silica bodies on the epidermis.

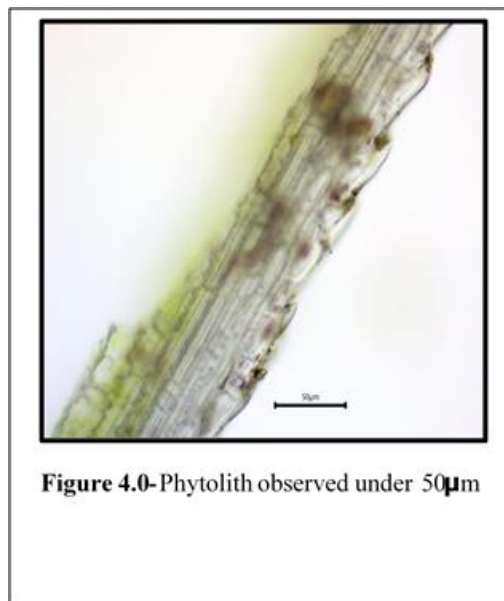


Figure 4.0-Phytolith observed under 50µm

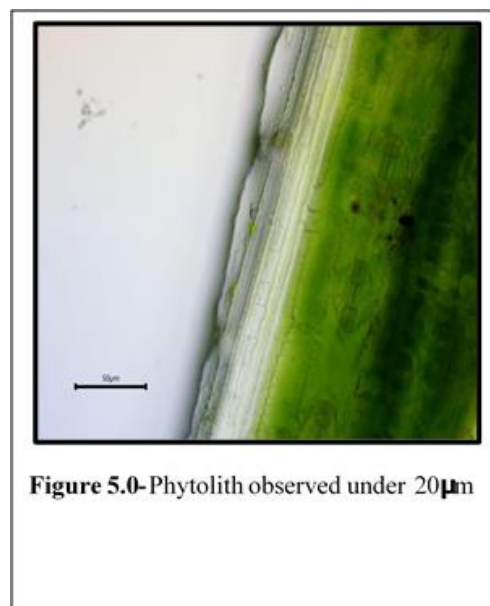


Figure 5.0-Phytolith observed under 20µm

## Materials and Method

### Materials used:

In the present study, Eleusine indica grass popularly known as Goosegrass is used. Fresh leaves are taken and cleaned so as to make them free from dust and mud particles and then washed with distilled water. Leaves are then sun dried till it loses its moisture and becomes brown and crispy. Dried leaves are stored in an air tight container, so that it does not absorb moisture from the environment.

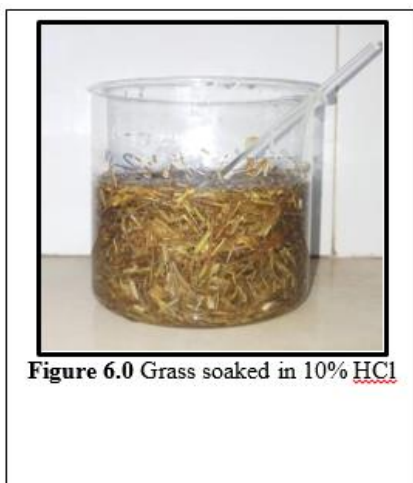
### Chemicals used:

The chemicals employed for removal of carbonates from the grass was acid, i.e. 10% Hydrochloric acid. Besides this, high concentration of acids are use as a mixture of 65% Nitric acid and 70% Perchloric acid in the ratio of 2:1. In the final step, 30% Hydrogen Peroxide is used for oxidation of Silica to obtain Silicon dioxide ( $\text{SiO}_2$ ).

**Methodology used:**

**(A) Extraction of Phytoliths**

The method employed for extraction of Phytoliths (Silica bodies) is Maceration method. In this method, a known quantity of sun dried leaves of Eleusine indica (Goosegrass) were taken. Cut these leaves into small pieces and soaked them in 10% Hydrochloric acid for 30 minutes to remove all the carbonates. After 30 minutes, rinsed these grass pieces and washed with distilled water till clear washings were seen. Then, air dried the grass pieces at room temperature.



After drying, transferred the grass in a round bottom flask and added 2:1 mixture of 65% Nitric acid and 70% Perchloric acid to it. Refluxed this at 80°C on a hot plate for 16 hours. After completion of 16 hours of refluxing, filtered the precipitate settled in the round bottom flask through Whatmann 41 filter paper.



Figure 7.0-Refluxing of grass with acid mixture

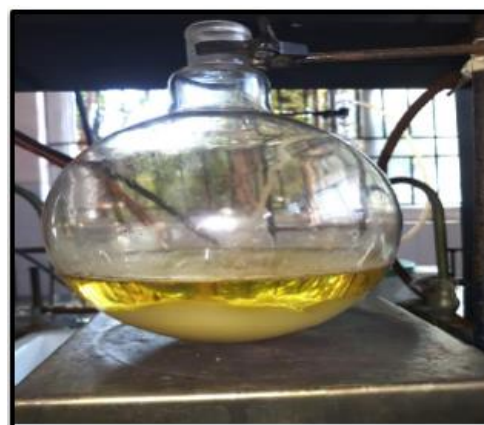


Figure 8.0-Phytoliths settled after refluxing

Washed the residue with distilled water till all the acid mixture was washed off from the residue and clear residue was obtained. The residue obtained in this process was Phytolith.

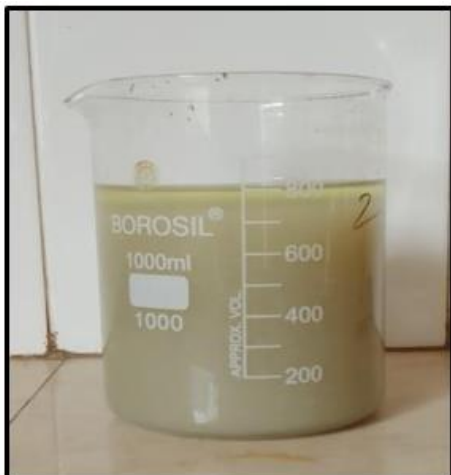


Figure 9.0-Washing of Phytoliths

To carry out synthesis of Silica, dried the Phytoliths obtained in the above process in the oven at 85°C for two days. After complete drying, transferred it in the crucible and incinerated it for two consecutive days till clear white compound was obtained. Cooled the compound and placed it in the muffle furnace for 4 hours at 500°C. After the muffle furnace was cooled, the compound was transferred in the round bottom flask. To this added 2:1 mixture of 65% Nitric acid and 70% Perchloric acid and refluxed it at 80°C on heating mantle for 16 hours. After completion of 16 hours of refluxing, cooled and filtered the compound using Whatmann 41 filter paper and rinsed with distilled water till all the acid mixture was washed away. Dried the residue completely in the oven at 85°C for two days. After complete drying, placed the compound in the crucible and incinerated for two days to obtain clear white silica. This was placed in the muffle furnace for 4 hours at 500°C for calcination. After calcination process, the obtained compound was Silica.

#### Oxidation of Silica

Further on, oxidation of Silica obtained in the above step was done. Transferred the Silica in a round bottom flask. To this, 30% Hydrogen peroxide was added and refluxed it at 80°C for 16 hours on a heating mantle. After completion of 16 hours, the solution was filtered through Whatmann 41 filter paper and rinsed 3 times with distilled water. Dried

the residue completely in the oven for two days at 85°C and placed in the crucible for incineration.



Figure 10.0-Oxidation of Silica

This was incinerated till clear white compound was obtained. After successful incineration, the crucible containing compound was placed in the muffle furnace for calcination for 5 hours at 500°C. After calcination, the obtained compound was Silicon dioxide (SiO<sub>2</sub>).

#### Characterization Methods:

Different characterization studies were employed to study the morphology and properties of synthesized Silicon dioxide (SiO<sub>2</sub>).

Confocal microscope was used for leaf blade observation, X-ray powder Diffraction (XRD) was used to study the crystal structure, Raman spectroscopy to identify molecules and study chemical bonding and intramolecular bonds. Infrared spectroscopy was used to determine functional groups in molecule, Energy Dispersive X-ray analysis was done to determine the chemical composition and Scanning Electron Microscopic images were obtained to study the morphology of synthesized Silicon dioxide (SiO<sub>2</sub>).

## IV. RESULTS AND DISCUSSION

The yield of silicon dioxide ( $\text{SiO}_2$ ) obtained from 20.0 grams of *Eleusine indica* leaves was 0.48 grams.

### Characterization Methods of $\text{SiO}_2$

**Confocal Microscopic images of Phytoliths in leaf blade of *Eleusine indica*:**

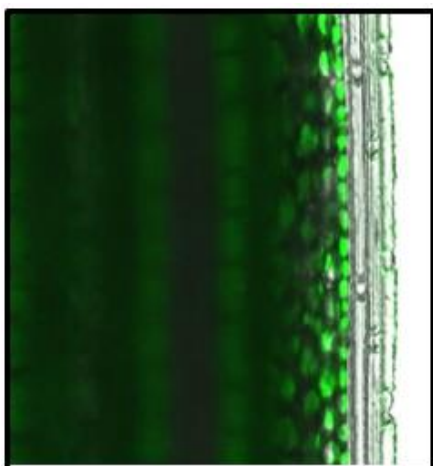


Figure 11.0-Phytoliths under  $50\mu\text{m}$

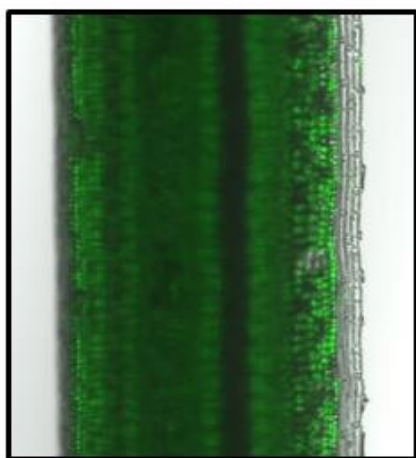


Figure 11.1-Phytoliths under  $100\mu\text{m}$

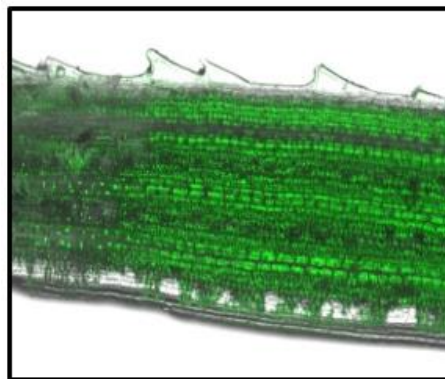


Figure 11.2 Phytoliths under  $200\mu\text{m}$

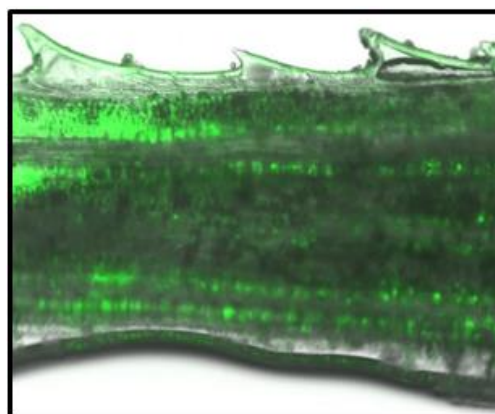
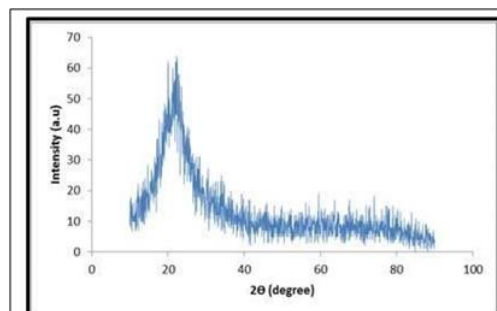


Figure 11.3 Phytoliths under  $100\mu\text{m}$

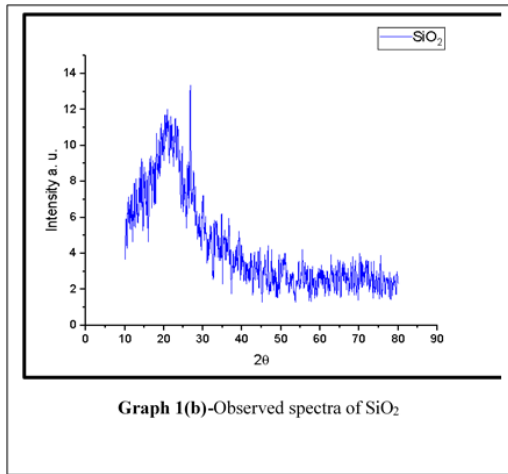
### X-ray Powder Diffraction (XRD): Reference XRD spectra of $\text{SiO}_2$ :



Graph 1(a)-Reference XRD spectra of  $\text{SiO}_2$

Source : <http://dx.doi.org/10.11113/mjfas.v13n3.593>

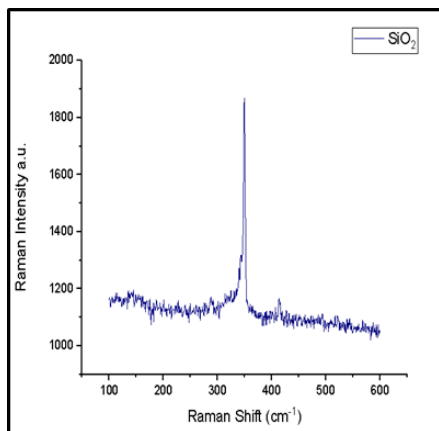
Observed XRD spectra of  $\text{SiO}_2$ :



XRD spectra of SiO<sub>2</sub> displayed a broad peak at 23° indicating the amorphous structure of SiO<sub>2</sub>.

**Raman Spectroscopy:**

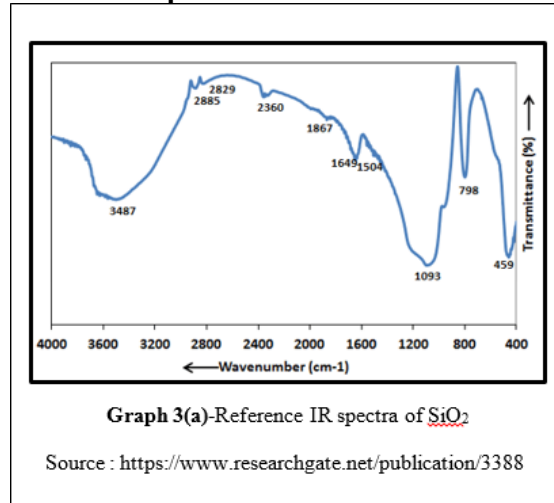
Observed Raman spectra of SiO<sub>2</sub>:



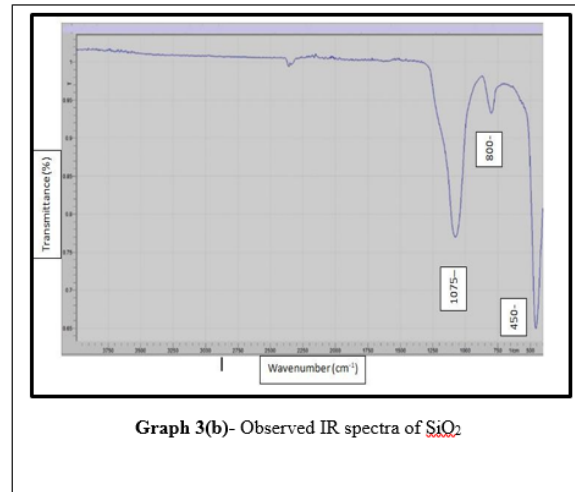
The band with the maximum at 350cm<sup>-1</sup> corresponds to D3 band assigned to scissoring in extended tetrahedron of amorphous SiO<sub>2</sub>.

**Infra-red spectroscopy of SiO<sub>2</sub>:**

**Reference IR spectra of SiO<sub>2</sub>:**



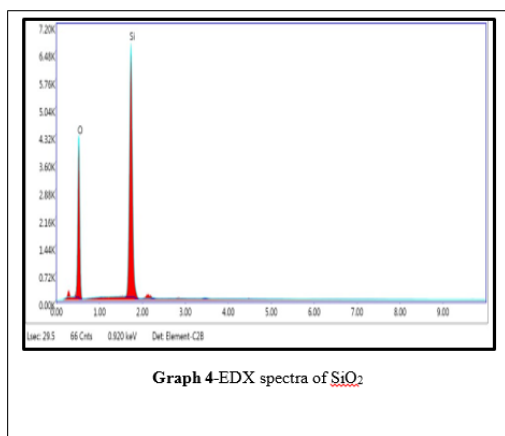
**Observed IR spectra of SiO<sub>2</sub>:**



**Transmittance O-Si siloxane.**

Less intense peak at 800 cm indicates Si-OH silanol bond. Intense peak at 450 cm indicates rocking vibrational band for SiO<sub>2</sub>.

**Energy Dispersive X-ray analysis (EDX):**



The elemental composition reported by EDX spectra confirms the presence of Silica and Oxygen in Silicon Dioxide (SiO<sub>2</sub>).

**Scanning Electron Microscopy (SEM):  
Observed SEM images of SiO<sub>2</sub>:**

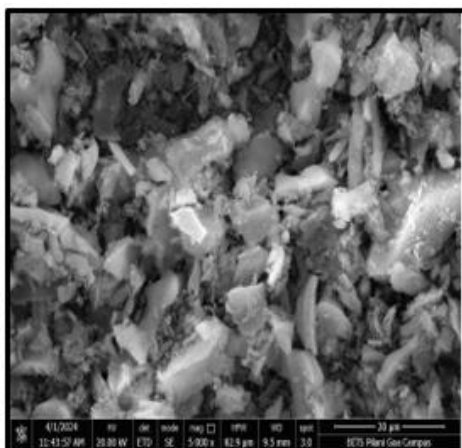


Figure 9.0-SEM image of SiO<sub>2</sub> showing 20µm particle observed at 5000x magnification

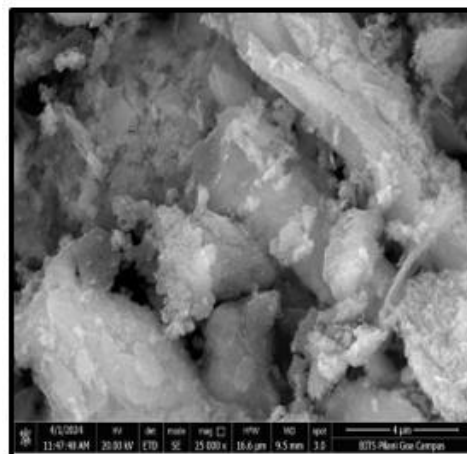


Figure 9.1-SEM image of SiO<sub>2</sub> showing 4µm particle observed at 25000x magnification

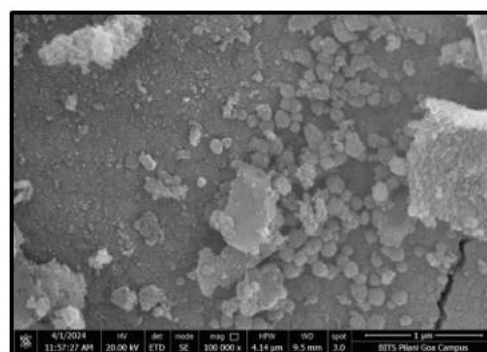


Figure 9.2- SEM image of SiO<sub>2</sub> showing 1µm particle observed at 100000x magnification

The observed SEM images of Silicon dioxide (SiO<sub>2</sub>) shows cluster formation of spherical particles of Silicon dioxide (SiO<sub>2</sub>).

**Discussion**

The dissertation aimed at green synthesis of Silicon dioxide particles from *Eleusine indica* leaves and to study its properties through several characterization methods.

During the course of this work, the foremost observation in methodology was evolution of toxic fumes during refluxing process of grass since it was carried out with concentrated acid mixture. The overall synthesis process was time consuming

because of long duration of refluxing process, filtration and drying of bulk phytoliths and also the oxidation process of Silica obtained. This makes it unfit for commercial and large scale production.

After first cycle of refluxing, when the filtration of obtained phytolith was carried out, it needed convenient size of filtration unit to avoid the loss of the desired product.

The obtained yield of Silicon dioxide (SiO<sub>2</sub>) was 0.48 grams from 20 grams of Eleusine indica leaves.

The silica content in plants differ depending on the species, topography where they are grown and its anatomy and other properties. So the entire botanical study of specific plant species should be carried out to confirm the source for desired amount of the final product.

## VI. CONCLUSION

The green synthesis of Silicon dioxide (SiO<sub>2</sub>) was carried out as they reduce the risk to the environment. The leaves of Eleusine indica (Crowfoot grass or wiregrass), belonging to Poaceae family, were observed under confocal microscope to confirm the presence of phytoliths (microscopic silica bodies). These phytoliths are responsible for silica content in grasses. For synthesis of Silica, the phytoliths were first extracted by refluxing the grass leaves with acid mixture of perchloric acid and nitric acid (2:1) for 16 hours at 80°C. Then, the conversion of obtained phytoliths to silica was carried out by again refluxing the extracted phytoliths with the same acid mixture for 16 hours at 80°C. Silicon dioxide (SiO<sub>2</sub>) was obtained on oxidation of synthesized Silica using hydrogen peroxide. The methodology involved long duration processes for completion of this procedure from extraction of phytoliths to oxidation of obtained Silica. The care was taken during filtration process to prevent the loss of the desired product. Calcination of synthesized SiO<sub>2</sub> was carried out effectively to prevent impurities and moisture content.

The yield obtained from 20 grams of Eleusine indica leaves was 0.48 grams.

Several characterization studies were carried out to study the appearance, bondings and properties of green synthesized Silicon dioxide (SiO<sub>2</sub>):

Confocal microscopic images of leaf blade confirmed the presence of Phytoliths in leaf anatomy of Eleusine indica.

X-ray powder diffraction spectra showed crystal structure with a broad peak at 23° which indicated the amorphous structure of SiO<sub>2</sub>.

Fourier Transform Infra-red (FT-IR) spectroscopy analysis was carried out to determine functional groups in SiO<sub>2</sub>. It produced a spectra with peaks at 1,075 cm<sup>-1</sup> indicating stretching bond between Si-O-Si siloxane, 800 cm<sup>-1</sup> indicated Si-OH silanol bond, 450 cm<sup>-1</sup> indicated rocking vibrational band for SiO<sub>2</sub>.

Raman spectroscopy was used to identify molecules and study chemical bonding and intramolecular bonds. The Raman spectra of synthesized SiO<sub>2</sub> which displayed a band with the maximum at 350cm<sup>-1</sup> corresponding to D3 band assigned to scissoring in extended tetrahedron in amorphous SiO<sub>2</sub>.

Scanning Electron Microscopic images were obtained to study the morphology of synthesized Silicon dioxide (SiO<sub>2</sub>). In the observed SEM images of SiO<sub>2</sub> shows cluster formation of spherical particles of Silicon dioxide (SiO<sub>2</sub>).

Energy Dispersive X-ray analysis done to determine the chemical composition of SiO<sub>2</sub> which confirmed silica and oxygen elements to be present in Silicon dioxide (SiO<sub>2</sub>).

### Future Scope

This study provides a portal for further research to identify more green sources of SiO<sub>2</sub> from Poaceae plant family existing in the environment as forgotten species.

One can focus on the study of semiconductor properties of SiO<sub>2</sub> for great applications in solar panels.

More studies and investigations could be considered like applications of SiO<sub>2</sub> in water filtration, biomedicine, adsorption processes.

Also comparative studies of SiO<sub>2</sub> synthesized in this method could be carried out by considering different types of Silica and several methodologies handed-down.

## REFERENCES

1. Currie, H. A., & Perry, C. C. (2007). Silica in Plants: Biological, biochemical and chemical studies. *Annals of Botany*, 100(7), 1383–1389. <https://doi.org/10.1093/aob/mcm247>
2. Firdaus, M., Osman, H., Metselaar, H. S. C., & Rozyanty, A. R. (2015). A Simple Method for the Production of Pure Crystalline Silica from Lemon Grass. *Bioresources*, 11(1).
3. Zarib, N. A., Abdullah, S., & Jusri, N. a. A. (2020). Effect of Acid Treatment on Extraction of Silica from Cogon Grass by Using C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> and HCL Acid. *IOP Conference Series: Materials Science and Engineering*, 834(1), 012067. Silicon, the long forgotten element by JG Barth.
4. Di Natale, F., Gargiulo, V., & Alfè, M. (2020). Adsorption of heavy metals on silica-supported hydrophilic carbonaceous nanoparticles (SHNPs). *Journal of Hazardous Materials*, 393, 122374. <https://doi.org/10.1016/j.jhazmat.2020.122374>
5. Tighadouini, S., Radi, S., Elidrissi, A., Haboubi, K., Bacquet, M., Degoutin, S., Zaghrioui, M., & Garcia, Y. (2019). Removal of toxic heavy metals from river water samples using a porous silica surface modified with a new  $\beta$ -ketoenolic host. *Beilstein Journal of Nanotechnology*, 10, 262–273. <https://doi.org/10.3762/bjnano.10.25>
6. Akhayere, E., Kavaz, D., & Vaseashta, A. (2019). Synthesizing Nano Silica Nanoparticles from Barley Grain Waste: Effect of Temperature on Mechanical Properties. *Polish Journal of Environmental Studies*, 28(4), 2513–2521. <https://doi.org/10.15244/pjoes/91078>
7. Bakar, R. A., Yahya, R., & Gan, S. N. (2016). Production of High Purity Amorphous Silica from Rice Husk. *Procedia Chemistry*, 19, 189–195. <https://doi.org/10.1016/j.proche.2016.03.092>
8. Kow, K. W., Yusoff, R., Raman, A. a. A., & Abdullah, E. C. (2014). Characterisation of bio-silica synthesised from cogon grass (*Imperata cylindrica*). *Powder Technology*, 254, 206–213. <https://doi.org/10.1016/j.powtec.2014.01.018>
9. Moftakhar, M. K., Dousti, Z., Yaftian, M. R., & Ghorbanloo, M. (2016). Investigation of heavy metal ions adsorption behavior of silica-supported Schiff base ligands. *Desalination and Water Treatment*, 57(56), 27396–27408. Silicon as a nutrient element for *Equisetum arvensel*. Ching-Hong Chen and Joyce Lewin <https://pubs.acs.org/sharingguidelines>
10. Yan, F., Jiang, J., Chen, X., Tian, S., & Li, K. (2014). Synthesis and characterization of silica nanoparticles preparing by Low-Temperature Vapor-Phase hydrolysis of SiCl<sub>4</sub>. *Industrial & Engineering Chemistry Research*, 53(30), 11884–11890. <https://doi.org/10.1021/ie501759w>
11. Synthesis of silica powders by pressured carbonation-X. Cai a, R.Y. Honga,b,\*, L.S. Wanga, X.Y. Wanga,c, H.Z. Li b, Y. Zheng d, D.G. Weia College of Chemistry, Chemical Engineering & Materials Science, and Key Laboratory of Organic Synthesis of Jiangsu Province, Soochow University.
12. Preparation of submicron spherical particles of silica by the water-in-oil microemulsion method. Wei Wang, Xiao-an Fu, Ji-an Tang, Long Jiang\* Institute of Photographic Chemistry, Academia Sinica, Beijing 100101, People's Republic of China.
13. Motomura, H., Fujii, T., & Suzuki, M. (2006). Silica Deposition in Abaxial Epidermis before the Opening of Leaf Blades of *Pleoblastus chino* (Poaceae, Bambusoideae). *Annals of Botany*, 97(4), 513–519. <https://doi.org/10.1093/aob/mcl014>
14. Lee, Y., Park, J., Oh, C., Oh, S., & Kim, Y. C. (2007). Preparation of highly monodispersed hybrid silica spheres using a One-Step Sol–Gel reaction in aqueous solution. *Langmuir*, 23(22), 10875–10878. <https://doi.org/10.1021/la702462b>
15. High-purification of amorphous silica originated from rice husks by combination of polysaccharide hydrolysis and metallic

- impurities removal. Junko Umeda, Katsuyoshi Kondoh\* General chemistry of Silica, L.T. Zhuravlev, 2009. [https://doi.org/10.1016/S0301-4770\(08\)60805-2](https://doi.org/10.1016/S0301-4770(08)60805-2)
16. Thermoluminescence (TL) response of silica nanoparticles subjected to 50 Gy gamma irradiation, Nik noor aien Mohamed Abdul Ghani, Izyan Hazwani Hashim, M. A. Saeed, 2017. <http://dx.doi.org/10.11113/mjfas.v13n3.593>
  17. Synthesis of SiO<sub>2</sub> Nanoparticles by Sol-Gel Method and Their Optical and Structural Properties. Sigamani Saravanan, R.S. Dubey Or Raghvendra S. Dubey, 2020. <https://www.researchgate.net/publication/3388>
  18. Synthesis of amorphous silica and sulfonic acid functionalized silica used as reinforced phase for polymer electrolyte membrane, Thanh Nhan Tran, Van Anh Van Pham, Phung ML Le, Thoa Nguyen, 2013. <http://dx.doi.org/10.1088/2043-6262/4/4/045007>
  19. Comprehensive review on uses of silicon dioxide in solar cell. A. S. Arul Prishya, Lalita Chopra, Manikanika, 2023. <https://doi.org/10.1016/j.matpr.2022.09.348>.
  20. Green and sustainable synthesis of silica nanoparticles. Sushilkumar A. Jadhav, P. S. Patil, Harshada Bhagawan Garud, 2021. <https://doi.org/10.1007/s41204-021-00124-1>