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## Preparing Nanosilica Particles from Rice Husk Using Precipitation Method

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### Abstract:

Nanosilica was extracted from rice husk, which was locally collected from the Iraqi mill at Al-Mishikhab district in Najaf Governorate, Iraq. The precipitation method was used to prepared Nanosilica powder from rice husk ash, after treating it thermally at 700°C, followed by dissolving the silica in the alkaline solution and getting a sodium silicate solution. Two samples of the final solution were collected to study the effect of filtration on the purity of the sample by X-ray fluorescence spectrometry (XRF). The result shows that the filtered samples have purity above 98%, while the non-filtered sample purity was around 96 %. The structure analysis investigated by the X-ray diffraction (XRD), found that the Nanosilica powder has an amorphous structure in nature. Also, it shows a broad peak at ( $2\theta = 22.25^\circ - 22.55^\circ$ ). The particle size distribution was determined by Atomic force microscope (AFM), the results gave that the average diameter equals 52.83 nm and dimension range in 30-75 nm, while B.E.T. analysis confirms a high surface area around 618 m<sup>2</sup>/g. FT-IR Spectra experimental data showed the presence of hydrogen-bonded silanol group (Si–O–H) and siloxane group (Si–O–Si) which proved the high purity of Nanosilica particles.

**Key words:** AFM, Nanosilica, Precipitation method, Rice husk, XRF.

### Introduction:

Silicon is a crystalline semi-metal that is covered about 30% of the Earth's crust, it is so widespread but difficult to find it as a pure state in nature, the only stable form of silicon at natural conditions is silicon dioxide (1). Silica is commonly named of silicon dioxide where it plays an important role in industries as raw material or enhanced them, such as the cement industry, glass, bottles and crockery, enamel, paints, ceramics, electronics, industrial tire, and even cosmetics. Technology development has increased in using silica at industries, especially with small size particles in microns and nanoscale which has better properties and improving its quality (2).

General Nanotechnology is the science that studies the phenomena and manipulation of materials at atomic, molecular, and macromolecular scales, where properties materials differ significantly from those at a larger scale. Nanomaterials have many applications as medical treatments, civil, health, fabrication, information, techniques, environments, and energy sources (3).

Nanosilica powder has received much attention because it has had high porosity and surface area,

thermal degradation that's making it used for a wide range of application such as in improving properties of concrete, ceramics, coatings, emulsifiers and biological sciences, stabilizers, pharmaceuticals, painting field, and insecticide industry (3,4).

Rice is the second main agricultural crop in the world after corn. The global annual product of rice husk as residues of rice cultivation is about 100 million tons per year (5). Most of the researches used different ways to recycled wastes and recovered composites and materials as an environmentally friendly reinforcing phase(6). They found the rice husk ash contains about 90 % of silica. Different economically methods can be used for the production of silica as gels and powders in nanoscale with highly porous, lightweight, and high superficial surface area, where they have new physicochemical properties which do not appear in the respective bulk materials (7). There are several methods to synthesis Nanosilica from rice husk: sol-gel method (8), precipitation method (9), calcination, or thermal method (10).

All the above methods are similar in converting the rice husk to ash, after that, it was burning at

550°C to 700°C amorphous structure is formed, while at temperatures higher than 700°C, the crystalline structure is formed (11). Sol-gel method involved simultaneous hydrolysis and condensation reaction, while the preparation method involves coagulation and precipitation silica from silica solution (12), the thermal method includes just the acid treatment step. This study aims to prepare pure Nanosilica from Iraqi rice husk ash by precipitation method and evaluated the characteristics of Nanosilica by using different techniques.

## Materials and Methods:

### Materials

The Rice husk tacked from the Iraqi mill at Al-Mishikhab District in Najaf Governorate has been used as a source of silica for Nanosilica particle synthesis. The chemicals substances included sodium hydroxide (NaOH powder) and hydrochloric acid (37% HCl) Germany-PanReac AppliChem, sulfuric acid (98% H<sub>2</sub>SO<sub>4</sub>) India-Thomas Baker.

### Rice Husk Ash Preparation

The collected Rice Husk has been washed thoroughly with distilled water to remove rice grains, sand, and other heavy impurities. It has been then dried in the oven at 105°C for 24 hours to remove the moisture. The Rice husk has been burned in an open environment to have Rice Husk Ash (RHA), the ash was collected and milled to get fine particles.

### Nanosilica Powder Synthesis Method

20 g of RHA was stirred with 120 mL of HCl (2N) for 2:30 hours at 80°C, then it was covered and left for 12 hours at room temperature to remove the metal impurities. Afterward, the acid was removed from RHA by filtration through filter paper (double rings No.103) with pore size 1-2.5 μm and washed with hot distilled water many times until the pH becomes approximately between 5.5-6.5. It was then dried in an electric oven at 105°C for 5 hours. The extracted RHA was burned inside a programmable furnace at 700°C for 5 hours until the disappearance of the black color which indicates the absence of carbon atoms and obtains pure white silica powder as shown in Fig.1.



Figure 1. White Silica Powder

10 g of the white Silica Powder was magnetically stirred with 80 ml of NaOH (2.5 N) for 3 hours at 95°C to form sodium silicate. The solution was filtered, and the residue was washed with distilled water 50 mL under continuous filtration. Then drops of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) were added with continuous stirring until the pH reached between 4-3.5 and silica gel was formed as shown in Fig. 2.

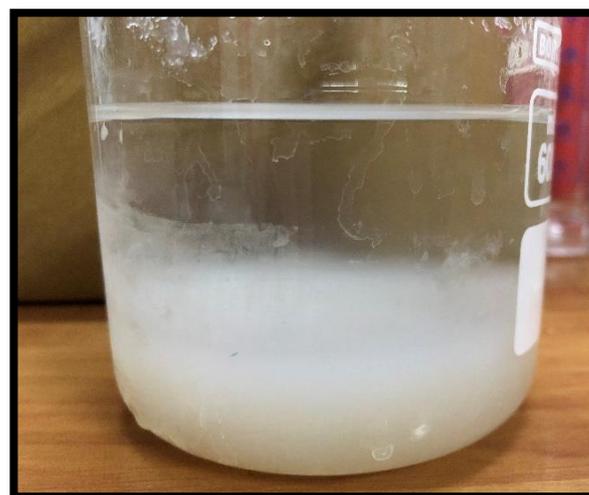
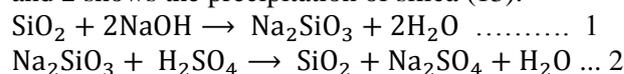


Figure 2. silica gel

The chemical reaction illustrated in equations 1 and 2 shows the precipitation of silica (13):



The precipitated silica was continuously washed with hot deionized water until the pH became between 7-7.5. The washing process continues for 6-7 days until increasing the pH, the produced was transferred into the oven and dried at 100°C for 12 hours to get a white powder which is silica

nanoparticle, and then collected for analysis as shown in Fig. 3.



Figure 3. silica nanoparticles

#### Characterization Methods:

#### Chemical Composition and Functional Groups Analysis of Nanosilica

The chemical composition of synthesized Nanosilica powder was determined by using the X-ray fluorescence spectrometry (SPECTRO XEPOS, Germany). While the functional groups that are existent on the silica surface identified by the FT-IR instrument (BRUKER, Germany).

#### Phase and Particle Size Analysis

The average diameter of Nanosilica was measured and imaged by an Atomic force microscope (AFM) (Type Angstrom, Scanning Probe Microscope, AA3000A°, U.S.A). While the phases contrast and composition measured by X-ray diffraction (type XRD-6000, Shimadzu, Japan) scan range is (10.0-60.65) degree scan, mode (continuous scan), scan speed (5.0 deg. / min).

#### Surface Area Measurement

The surface area properties of nanoparticles were measured by Brunauer-Emmett-Telle (BET) analysis (Q Surf 1600, USA) range (0.01-2000 m<sup>2</sup>/mg).

#### Results and Discussion:

#### Composition of Nanosilica Extract

Table 1 illustrates the XRF analysis of chemical contents and purity of Nanosilica at 700°C for 5 hours. Two samples were used before and after filtration of sodium silicate collected from treated silica with NaOH (2.5N).

Table 1. Elemental Composition of nanosilica

Elemental Component (wt.%)	Before filtration	After filtration
SiO <sub>2</sub>	96.12	98.9
Fe <sub>2</sub> O <sub>3</sub>	0.16	0.02
Al <sub>2</sub> O <sub>3</sub>	0.04	0.0041
CaO	0.53	0.121
MgO	0.09	0.0037
P <sub>2</sub> O <sub>5</sub>	0.83	0.54
TiO <sub>2</sub>	0.128	0.0031
SO <sub>3</sub>	0.812	0.411
ZnO	0.0026	0.0025
K <sub>2</sub> O	0.17	0.0013
others	1.027	0.03

It is clear that the major component of both Nanosilica samples is SiO<sub>2</sub>, the purity of the sample before filtered was 96.12%, while the purity reached 98.9% for the filtered sample. The purity of the sample before filtration was less than the filtered sample due to the presence of impurities that was not removed during the pretreatment of the sample. These results agreed with (12,13, 8). Figure 4 shows the residue on filter paper.

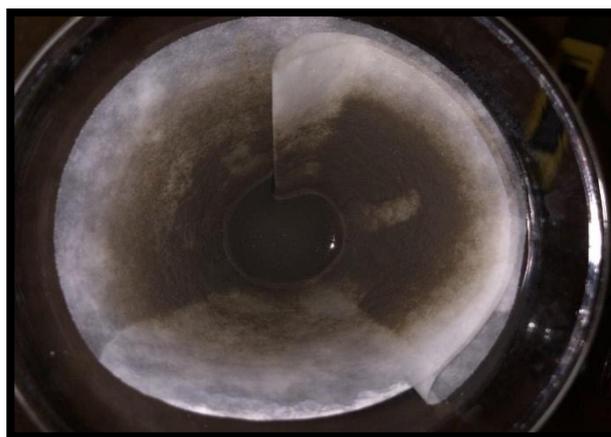


Figure 4. The residue on filter paper.

#### Structure of Nanosilica

The X-ray diffraction of Nanosilica was used to evaluate the crystalline form. A crystalline is composed of regularly arranged in a 3D zone. In contrast, amorphous materials have an unregular arrangement and atoms are randomly distributed in the 3D zone. The scattering of X-rays by atoms can be considered to determine the predominant shape of the atoms where a regular arrangement of atoms exposed to X-ray will only be dispersed in certain directions and cause high-intensity peaks, this means that the material has a crystalline form (14).

However, when X-ray dispersed in different directions leading to a large bump have a shape similar to a hill, the peak in the range  $(2\theta) = 15^\circ-30^\circ$ , this indicating the presence of amorphous structure and a highly disordered form of silica, Amorphous phase will be prevalent (8). Figure 5 shows the maximum intensity of a broad peak at  $2\theta$  between  $22.25^\circ-22.55^\circ$  as an indication for the absence of any crystalline form. Eventually, the results proved that the sample has an amorphous nature of silica. The crystalline form of silica is considered a defect in preparing silicon-based materials, where it makes it inactive (15).

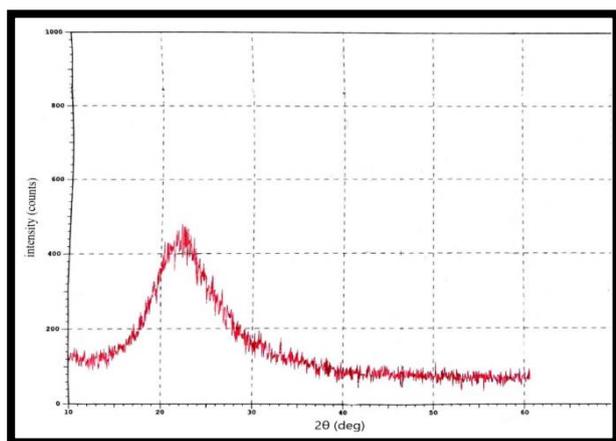


Figure 5. The X-ray diffraction of the Nanosilica

### Surface Area of Nanoparticles

The B.E.T. analysis of nanoparticles is an important parameter since materials with high surface areas have high surface energy and high activity at different applications (15). However, the surface area of Nanosilica extracted from biomass depending on the type of treatment method, the extraction methods, sodium silicate concentration, washing, pH adjustment, temperature, and burning time (9). The specific surface area was determined by the B.E.T. method, where the BET result at  $700^\circ\text{C}$  and acid-bases treated of RHA was  $618\text{ m}^2/\text{g}$

and this result are approximately in agreement with the results studied by (8).

### Particles Size of Silica Nanoparticles

Atomic force microscope (AFM) was used for measuring the diameter of silica nanoparticles that chemically produced. The diameter is affected by four parameters: NaOH concentration, pH, silica stirred time with NaOH, and nanoparticle drying time (2,5). The average diameter of Nanosilica powder resulted from using NaOH (2.5N) for 3 hours was 52.83 nm. The highest volume ratio of particle size distribution was 16.36% with a diameter of 60 nm, while the lowest percentage volume ratio was 1.58% with a diameter of 30 nm. The result of the scanned area gives the topography of Nanosilica particles, where it showed the aspherical shape and small grains in agglomerated form. The particle size distribution and the scanned area of silica nanoparticles are shown in Table 2 and Fig. 6.

Table 2. particle size distribution

Diameter (nm)	Volume (%)	Cumulation (%)
30	1.58	1.58
35	7.39	8.97
40	6.86	15.83
45	11.08	26.91
50	14.78	41.69
55	11.87	53.56
60	16.36	69.92
65	11.61	81.53
70	10.55	92.08
75	7.92	100

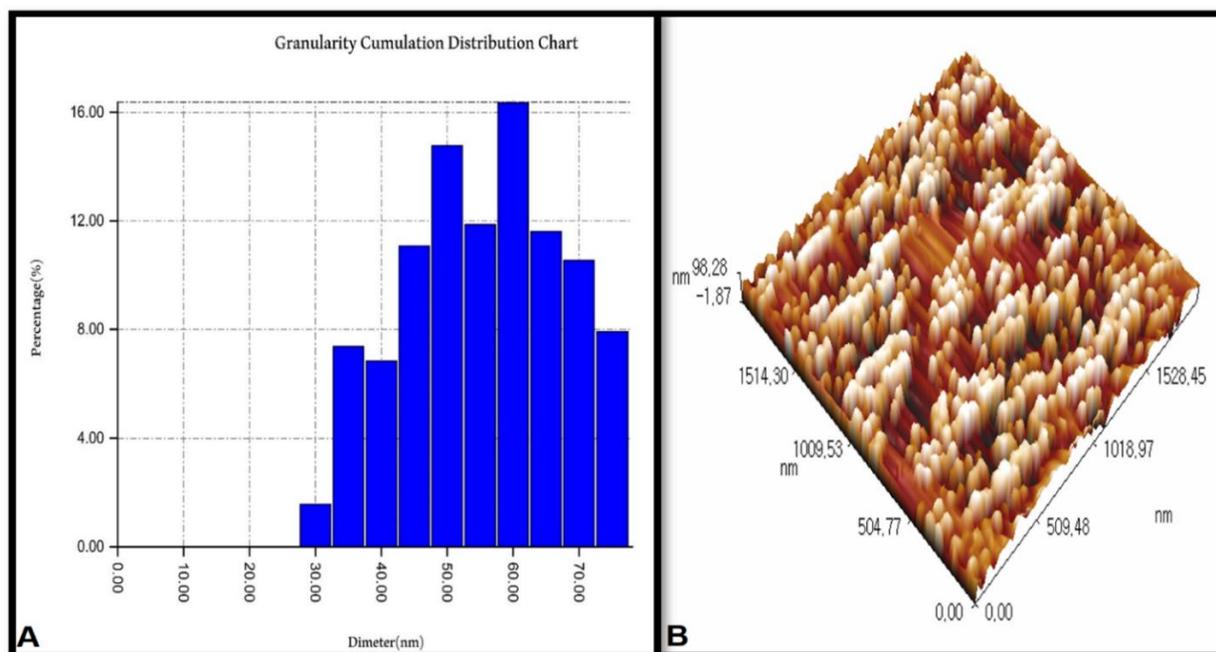


Figure 6. AFM analysis A) Particles size distribution B) Scanned area of silica nanoparticles

### Functional Groups Analysis

FT-IR Spectra measurement of synthesized silica nanoparticles was done to characterize the functional groups that are existing on the surface in the range of 4000–400  $\text{cm}^{-1}$ . Where the existence of adsorbed water and silanol groups as well as siloxane linkages can be easily recognized. Figure 7 shows the dominant peak at 1107.06  $\text{cm}^{-1}$  where it can be attributed to Si–O–Si asymmetric vibration which is concerning with the arrangement of dense silica organize (16,15). The band at 808.1  $\text{cm}^{-1}$  is due to the symmetric vibration of the Si–O–Si bond (17). The peak 952.77  $\text{cm}^{-1}$  indicates of presence of Si–O stretching vibration of the silanol group. The peak appeared at 474.46  $\text{cm}^{-1}$  is related to the bending vibration of the Si–O–Si bond (18). The bending vibration at 3452.34 and 1633.59  $\text{cm}^{-1}$  were due to the H–O–H, stretching of different hydroxyl groups of adsorbed water molecules on the silica surface which reflected the high purity of precipitated Nanosilica and give adsorption characteristic of particles (6). The band peaks between 4000-400  $\text{cm}^{-1}$  are the main indicator of the silica material, which represents the successful production of silica nanoparticles from rice husk (19).

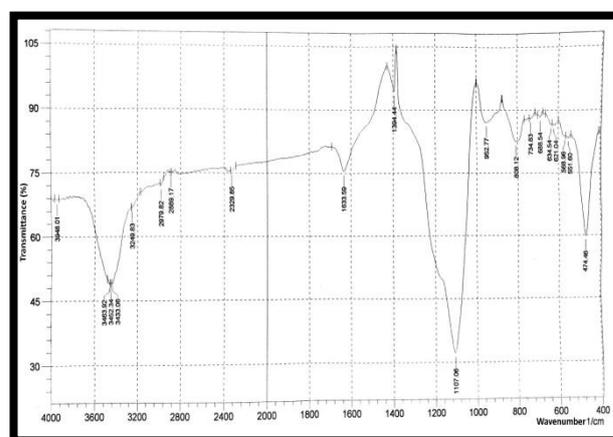


Figure 7. FT-IR spectra of synthesized silica nanoparticles

### Conclusions

- High Pure Nanosilica has been successfully extracted from rice husk as an environmentally friendly methodology of converting waste to active material used in different applications.
- Silica nanomaterial has been prepared by cheap and simple methods followed by three-stages; acid treatment, thermal treatment at 700°C, and precipitation method.
- The analysis of the silica nanomaterial shows an amorphous structure with a maximum intensity of peak at 2θ between 22.25°- 22.55°. Also, it has a higher purity of more than 98% and the average particle diameter was 52.83 nm, and the specific surface area was 618  $\text{m}^2/\text{g}$ .
- The mesoporous structure of Nanosilica particles makes it a promising material that can be used as

an adsorbent of contaminants, in addition to its useful physical and mechanical properties.

#### Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

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## تحضير جسيمات السيليكا النانوية من قشر الأرز العراقي بطريقة الترسيب

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### الخلاصة:

تم استخلاص جزيئات النانو سيليكيا من قشر الأرز، والتي تم جمعها محلياً من المطحنة العراقية الواقعة في منطقة المشخاب في محافظة النجف جنوب العراق. تم استخدام طريقة الترسيب لتحضير مسحوق نانو سيليكيا من رماد قشر الأرز، بعد معالجته حرارياً عند درجة حرارة 700 درجة مئوية، وتبعه إذابة السيليكا في محلول قلوي للحصول على محلول سيليكات الصوديوم. جمعت عينتان من المحلول النهائي لدراسة تأثير الترشيح على نقاء العينة بواسطة مطياف فلورية الأشعة السينية (XRF). أوضحت النتائج أن العينة التي تم ترشيحها تمتلك نقاوة بنسبة اعلى من 98٪، بينما كانت نقاوة العينة الغير مرشحة ما يقارب 96٪. وجد تحليل البنية السطحية بواسطة حيود الأشعة السينية (XRD) أن مسحوق النانو سيليكيا له بنية غير متبلورة في طبيعتها. أيضاً، اظهر ذروة واسعة عند  $(2\theta = 22.25^\circ - 22.55^\circ)$ . تم تحديد توزيع حجم الجسيمات بواسطة مجهر القوة الذرية (AFM)، ووضحت النتائج أن متوسط القطر (52.83 نانومتر) ونطاق القطري في حدود (30-75 نانومتر)، بينما أكد تحليل B.E.T ان لجزيئات النانو سيليكيا مساحة سطح عالية 618 م<sup>2</sup>/غم. أظهرت البيانات التجريبية لـ FT-IR Spectra وجود مجموعة سيلانول مرتبطة بالهيدروجين (Si-O-H) ومجموعة سيلوكسان (Si-O-Si) والتي تثبت النقاوة العالية لجزيئات النانو سيليكيا.

الكلمات المفتاحية: نانو سيليكيا، قشر الأرز، طريقة الترسيب، AFM، XRD.