Extraction of high purity amorphous silica from rice husk by chemical process

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Abstract. High purity amorphous silica (SiO₂) is extracted from agriculture waste (rice husk) that supplied from Al-Najaf province, Iraq. Silica is the major inorganic constituent of the rice husk. It is prepared with using acid pretreatment of (3N HCl), then burned it at (700°C) for 4 hrs, and followed with leaching process by 1.5, 2, 2.5, and 3N NaOH. The extracted results are high-surface area of amorphous silica particles. Extracted results are silica particles were high surface area of amorphous silica particles. These particles were characterized by X-Ray diffraction (XRD), and X-Ray Fluorescence (XRF) and Atomic force microscopy (AFM) techniques. High pure amorphous silica observed from rice husk ash was confirmed by XRD diffraction. The silica purity results measured by X-Ray fluorescence was 99.714% for leaching at 3N NaOH. Results from (AFM) of silica with nanoscale sizes and microparticles with diameters ranging from (87-114) nm.

Keywords: silica (SiO₂), leaching, rice husk ash (RHA), rice husk (RH)

1. Introduction
Silica has been successfully extracted from different agricultural wastes like rice husk [1-5], sugar cane bagasse [6, 7], coffee husk [8], wheat husk [9] and corn cob [10, 11]. Rice husks are major waste products of the agricultural industries. In recent years, agricultural products and by products (waste) attract towards sustainable energy generation, it is considered as a potential raw material for preparing high-value products like silicon composite [12-13]. Silicate materials can be found in two forms, crystalline and amorphous. High purity amorphous silica (SiO₂) from renewable sources has huge industrial applications, it can be used in completely different materials, such as paints, catalysts, lithium batteries, absorbents [3, 6]. Also, it is used in rubber, plastics, coating, electronics, optics, and refractories. Silica in crystalline form is widely used in glass and ceramic industry, etc. [1, 2, 12]. One of the most important techniques used to prepare nano-silica is the simple chemical extraction process [1, 13]. Lately, much attention has been focused on the use of high-purity silica powder preparation from rice husk. The purity and colour of the ash are usually impacted through a variety of metal ions as well as unburned carbon [12-13]. Another method of silica production is a sol-gel process but it is expensive due to high material cost [14]. Mohanraj et al. (2012) [10] prepared and characterized amorphous SiO₂ from rice husk ash by precipitation method. Using a simple chemical technique has a benefit of producing valuable silica particles at a lower cost. In this study, High purity amorphous silica extract is obtained from rice husk using a different concentration of sodium hydroxide. This highly purified amorphous silica has a promising future as biomaterials because it comes from biomass. Silica-based materials are frequently used in various biological applications due to their effectiveness in bioactivity and characterization of biodegradation.
2. Experimental Work

2.1. Materials
The raw rice husk (RH) was obtained from Al-Najaf province -Iraq. Table 1 shows the chemical composition of rice husks (RH). Other chemicals such as ammonium hydroxide NH₄OH, sodium hydroxide NaOH were imported from Fluka, Germany and hydrochloric acid (35%) was obtained from Merck, India. Initially, locally collected rice husk waste is cleaned by washing with distilled water to remove adhering soil and other contaminations present in them and then it dried by exposing it to sunlight for 24 hrs.

Table 1. The chemical composition of raw rice husk.

| Main Constituents | wt%   |
|-------------------|-------|
| Hemi cellulose    | 20.2 - 24.3 |
| Cellulose         | 34.4 - 38.6  |
| Lignin            | 19.2 - 19.8  |
| Ash Silica        | 18.7   |
| Metallic oxides   | 0.39 (MgO, Al₂O₃, CaO, K₂O, NaO) |

2.2. Pre-Treatment of Rice Husk
The first step of extraction the high purity amorphous silica (SiO₂) is started by acid leaching for 100g of rice husk. It is refluxed with an acidic solution carried out at 500 ml of 3N HCl using heating mantle and stirrer for 4 hrs at 80°C in a glass-bottomed round bottle flask. After the acid leaching process, the acidic solution is washed repeatedly in distilled water until the filtrate has become free from acid than dried in an oven at 100°C for 6 hrs. The leaching reactor is (3) liters glass beaker with a mechanical mixer. The experimental set-up for the leaching process is shown in Figure 1. The rice husk with pre-treatment is designated as (RH’).

2.3. Calcination Treatment
100 grams of each agricultural waste sample (RH’) is calcinated (thermal decomposition) at a temperature of 700°C. The pyrolysis process is achieved in a furnace (Lenton furnace, UK) for 4 hrs at a heating rate of 10°C min⁻¹. The powder obtained is designated as (RHA).

2.4. Chemical Process of High Purity Silica
To prepare high purity silica, the following stages are used:

i. 20 grams of RHA sample was stirred in 160 mL of (1.5, 2, 2.5, 3) N (NaOH) and heated at 80°C for 3 hrs in a covered 250 mL glass beaker. The obtained results were titrated slowly with an acid solution. The mixture solution is stirred in the Erlenmeyer flask using a magnetic agitator as shown in Figure 2. The residue solution is obtained by filtering the dissolved RH solution with Whatman filter paper (No. 41 without ashless) and at the same time, it is thoroughly washed with boiling water (100 ml) to obtain sodium silicate solution, as shown in Figure 3. This solubility can be described by the following equation (1)[7]
ii. The sodium silicate solution is titrated with 5N H$_2$SO$_4$ under constant stirring rate (1000 r.p.m.) to precipitate dissolved silicate in the form of white gelatinous, as illustrated in the reaction below.

\[
\text{Na}_2\text{SiO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{SiO}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \quad (2)
\]

The solution of pH is monitored and the titration process is stopped at pH 2 to produce silica gel (SG). After the gelatin gel occurs, add an NH$_4$OH solution until the pH reaches 8.5. After that, ageing is allowed to stand at room temperature for 4 hrs. The formed gel is frequently washed with deionized water to be free of any chemical additives and filtered through Whatman (No. 41 ashless) filter paper by vacuum filtration pump.

iii. The silica gel (SG) residue washed with 20 ml warm deionized water at 45°C, allow to cool down at room temperature.

\[
\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \quad (1)
\]

**Figure 2.** Reflux with a chemical process.

The precipitated silica gel (SG) is washed repeatedly with warm deionized water at 45 °C until it is obtained completely alkali free. At the end of the extraction process, the insoluble residue was separated from the solution by a Buchner funnel equipped glassy. Buchner flask and vacuum pump (VALUE-VE115N) with filtration paper (15 cm diameter) are shown in Figure 3.

**Figure 3.** Buchner funnel equipped (vacuum filtration).

The residues are collected and dried at 100°C for 12 hrs in the oven. The end product is white silica stored in sealed plastic bags. Figure 4 shows a flow chart of preparation steps by precipitation method to produce high purity-silica.
3. Results and Discussion

3.1. Effect of the NaOH Solution Concentration on the Purity of Silica Powder

To obtain silica, RHA was solubilized by reacting with intense alkali and the result was water-soluble sodium silicate (Na$_2$SiO$_3$), the filtered sodium silicate solution was transparent. Silicon dioxide reacts with hot concentrated alkali or fused hydroxide, as shown in equation (1). The presence of Na$^+$ ion has an important role in this reaction. The interaction between Na$^+$ ion and negative silicate ions would accelerate the reaction [15]. Silica gradually deposited and lead to gel formation over 24 hrs. The resulting silica gel was fragmented and washed frequently with deionized water until sodium sulfate-free. Silica gel is filtered in Figure 5-a and is followed directly by drying in an oven at 100$^\circ$C. Dried silica will appear as a fine and white powder, as shown in Figure 5-b.

![Figure 5. Silica nanoparticle production process: a) precipitated silica gel, b) silica particles.](image)

It was found that the produced silica particles were spherical, agglomerated. The change in silica particles can be caused by the change from the ratio of the concentrations ammonia NH$_3$OH and the H$_2$SO$_4$ solution. At these steps, high purity silica was obtained.

3.2. XRF Analysis

X-Ray Fluorescence (model-Shimadzu-XRF-7000, US) is used to quantitatively investigate the level of impurities in silica (SiO$_2$) and evaluate the purification effect. Table 2 shows typical XRF analysis for high purity amorphous silica (SiO$_2$) particles, which clearly have higher purity of the silica extracted at a various ratio of sodium hydroxide. It shows that the best results of high purity with 3N NaOH treatment that affect the removal of metallic components.
Table 2. XRF present in the high purity amorphous silica (SiO$_2$) From (RH) at calcination temperature of 700°C for 4 hrs.

| Components as oxides | 1.5N NaOH | 2N NaOH | 2.5N NaOH | 3N NaOH |
|----------------------|-----------|---------|-----------|---------|
| SiO$_2$              | 98.192    | 99.204  | 99.642    | 99.714  |
| K$_2$O               | 0.140     | 0.062   | 0.025     | 0.005   |
| Fe$_2$O$_3$          | 0.462     | 0.152   | 0.104     | 0.092   |
| CaO                  | 0.104     | 0.039   | 0.036     | 0.029   |
| Cr$_2$O$_3$          | 0.093     | 0.063   | 0.053     | 0.017   |
| MnO                  | 0.063     | 0.057   | 0.025     | 0.011   |
| P$_2$O$_5$           | 0.718     | 0.331   | 0.092     | 0.110   |
| Others               | 0.228     | 0.092   | 0.023     | 0.022   |

3.3. X-Ray Diffraction (XRD)

The structure of high purity amorphous silica (SiO$_2$) was investigated using X-ray diffraction (LabX-XRD-6000) as shown in Figure (6-a, b, c, and d). These figure display one strong broad peak at 2θ = 22° which confirms the amorphous nature of silica. The lack of sharp peaks indicates the absorbance of any ordered crystalline structure in the prepared silica at the treated NaOH solution. Figure 6 shows an XRD pattern of high purity silica powder in the range of 2θ = 0°-90°. A broad peak was observed at 2θ = ~17°-29° corresponding to the formation of amorphous silica according to standard patterns of silica in Standards Joint Committee on Powder Diffraction (JCPDS-card # 96-412-4080). It can be concluded that the absence of any ordered crystalline structure is observed. The degree of purity of amorphous silica can be diagnosed or observed by studying the effect of the difference in the concentration of sodium hydroxide on its extraction process, as shown in Figure 6-a, b, c, and d. It reveals that changes in the concentration of sodium hydroxide have affected the purity of silica. This result reveals that RHA samples treated with various types of chemical materials do not affect the crystalline structure of products. From Figure 6, it can be seen that the obtained curves were completely amorphous and the degree of smoothness of the curves increased with increasing NaOH concentration from 1.5N to 3N. This result is completely agreed with the fact that sodium hydroxide only dissolves amorphous silica, the result achieved was agreed with Ritu Payal et al., 2017., Ahmed A. Moosa, Ban F. Saddam, 2016, and Nittaya and Apinon, 2008[17, 2, 18].
3.4. Surface Morphology Analysis by (SEM)

SEM images (Vega 3, TESCAN, USA) given in Figure 7 shows the morphology of silica particles synthesized from RHA by calcination at 700°C and pre-treatment with 3N HCl. It was precipitated with different concentrations of 1.5, 2, 2.5, and 3N NaOH solutions. According to the SEM images of silica precipitated at 1.5N NaOH, the extracted silica was spherical and agglomerated form. The silica synthesized in 2.5 and 3N NaOH solution is more agglomerated from the silica at 1.5 and 2N NaOH solution. The silica particles of all samples were irregular and amorphous. These particles show a tendency to form bigger particles (aggregates). Although different concentrations of sodium hydroxide have affected the obtained silica composition, the structure and morphology of these molecules have not changed.
Figure 7. SEM images of silica at varied NaOH concentrations, (a) 1.5 N (b) 2 N, (c) 2.5 N, and (d) 3 N.

3.5. Atomic Force Microscopy (AFM) Analysis
Atomic force microscope (type angstrom, scanning probe microscope, advanced Inc, AA 3000A°, USA) observations identified the diameters of prepared extraction high purity amorphous silica (SiO$_2$) in 1.5, 2, 2.5, and 3N NaOH solutions are in range (87-114) nm. Four different groups of samples were analysed, the range at (1.5N NaOH) was (60–190) nm, with an average diameter of 87.91 nm, as shown in Figure (8- a, b, and c) and Table (3). The range at (2N NaOH) was (70–165) nm, an average diameter of 88.93 nm, as shown in Figure (9- a, b, and c) and Table 4. The range at (2.5N NaOH) was (90–170) nm, an average diameter of 105.71 nm, as shown in Figure (10- a, b, and c) and Table 5. The range at (3N NaOH) was the (80–230) nm, an average diameter of 113.63 nm and higher volume percent of particle size was 16.5 nm as shown in Figure (11- a, b, and c) and Table 6. According to the results of particle size in (AFM), the size distribution of silica particles was in four main different size groups, based on the extraction conditions. It can be concluded that the particle sizes range from (87.91-114.63) nm depends on concentrations of NaOH solution.
Table 3. The particle size distribution of silica extracted using 1.5N NaOH solution.

| Diameter (nm) | Volume (%) | Cumulation (%) | Diameter (nm) | Volume (%) | Cumulation (%) | Diameter (nm) | Volume (%) | Cumulation (%) |
|---------------|------------|----------------|---------------|------------|----------------|---------------|------------|----------------|
| <=50%         | <=10%      | <=90%          |               |            |                |               |            |                |
| 60.00         | 5.06       | 5.06           | 100.00        | 4.43       | 74.37          | 140.00        | 2.22       | 96.52          |
| 65.00         | 14.87      | 19.94          | 105.00        | 4.75       | 79.11          | 145.00        | 0.63       | 97.15          |
| 70.00         | 10.44      | 30.38          | 110.00        | 2.85       | 81.96          | 155.00        | 0.95       | 98.10          |
| 75.00         | 6.96       | 37.34          | 115.00        | 3.80       | 85.76          | 160.00        | 0.95       | 99.05          |
| 80.00         | 5.06       | 42.41          | 120.00        | 4.11       | 89.87          | 170.00        | 0.32       | 99.37          |
| 85.00         | 9.49       | 51.90          | 125.00        | 1.90       | 91.77          | 175.00        | 0.32       | 99.68          |
| 90.00         | 8.54       | 60.44          | 130.00        | 1.90       | 93.67          | 190.00        | 0.32       | 100.00         |

Figure 8. AFM for silica extracted using 1.5 NaOH solution, a) 3D morphology, b) 2D morphology, c) particle size distribution.

Table 4. The particle size distribution of silica extracted using 2N NaOH solution.

| Diameter (nm) | Volume (%) | Cumulation (%) | Diameter (nm) | Volume (%) | Cumulation (%) | Diameter (nm) | Volume (%) | Cumulation (%) |
|---------------|------------|----------------|---------------|------------|----------------|---------------|------------|----------------|
| <=50%         | <=10%      | <=90%          |               |            |                |               |            |                |
| 70.00         | 12.22      | 12.22          | 100.00        | 6.67       | 76.67          | 130.00        | 2.22       | 97.22          |
| 75.00         | 18.33      | 30.56          | 105.00        | 5.00       | 81.67          | 145.00        | 0.56       | 97.78          |
| 80.00         | 11.11      | 41.67          | 110.00        | 1.67       | 83.33          | 150.00        | 0.56       | 98.33          |
| 85.00         | 13.33      | 55.00          | 115.00        | 7.22       | 90.56          | 155.00        | 0.56       | 98.89          |
| 90.00         | 7.22       | 62.22          | 120.00        | 1.11       | 91.67          | 160.00        | 0.56       | 99.44          |
| 95.00         | 7.78       | 70.00          | 125.00        | 3.33       | 95.00          | 165.00        | 0.56       | 100.00         |
Figure 9. AFM for silica extracted using 2N NaOH solution, a) 3D morphology, b) 2D morphology, c) Particle size distribution.

Table 5. The particle size distribution of silica extracted using 2.5N NaOH solution.

| Diameter (nm) | Volume (%) | Cumulation (%) | Diameter (nm) | Volume (%) | Cumulation (%) | Diameter (nm) | Volume (%) | Cumulation (%) |
|--------------|------------|----------------|--------------|------------|----------------|--------------|------------|----------------|
| <=50%        | <=10%      | <=90%          |              |            |                |              |            |                |
| 90.00        | 19.05      | 19.05          | 120.00       | 11.90      | 80.36          | 150.00       | 3.57       | 98.21          |
| 100.00       | 26.19      | 45.24          | 130.00       | 10.71      | 91.07          | 160.00       | 1.19       | 99.40          |
| 110.00       | 23.21      | 68.45          | 140.00       | 3.57       | 94.64          | 170.00       | 0.60       | 100.00         |
Figure 10. AFM for silica extracted 2.5N NaOH solution, a) 3D morphology b) 2D morphology c) Particle size distribution.

Table 6. The particle size distribution of silica at using 3N NaOH solution.

| Diameter (nm) | Volume (%) | Cumulation (%) | Diameter (nm) | Volume (%) | Cumulation (%) | Diameter (nm) | Volume (%) | Cumulation (%) |
|---------------|------------|----------------|---------------|------------|----------------|---------------|------------|----------------|
| <=50%         | <=90%      | <=99%          |               |            |                |               |            |                |
| 80.00         | 3.88       | 3.88           | 130.00        | 10.19      | 74.27          | 180.00        | 1.46       | 99.03          |
| 90.00         | 16.02      | 19.90          | 140.00        | 8.25       | 82.52          | 200.00        | 0.49       | 99.51          |
| 100.00        | 16.50      | 36.41          | 150.00        | 7.77       | 90.29          | 230.00        | 0.49       | 100.00         |
| 110.00        | 15.05      | 51.46          | 160.00        | 4.37       | 94.66          |               |            |                |
| 120.00        | 12.62      | 64.08          | 170.00        | 2.91       | 97.57          |               |            |                |
Figure 11. AFM for silica extracted using 3N NaOH solution, a) 3D morphology b) 2D morphology c) Particle size distribution.

It is observed from Figure 12 that with an increase in the concentration of sodium hydroxide, the particle size of the extracted silica increases. Hence, the surfaces of SiO$_2$ particles tend to be rough with an increase in the concentration of NaOH solution, the particles are decomposed and the distribution of the particles is inhomogeneous. The agglomerated of silica particles have resulted from Van Der Walls forces which act to aggregate the particles. This agrees with the research of Silviana et al., 2018 [15].

Figure 12. The relationship between particle size and NaOH concentration.

4. Conclusions
The research conclusions can be presented in the following points:
i. The amorphous and white silica has been successfully extracted from the rice husks in Iraq using a precipitation technique
ii. Pre-treatment process in 3N HCl for RH before the extraction process is an essential process to reduce the percentage of impurities in agricultural waste.

iii. The best result at extracted with 3N NaOH at 700 °C for 4 hrs was an amorphous white colour powder of silica with particle shape uniform and agglomerated.

iv. Leaching process at difference NaOH concentrations plays an important role in final purity for silica. The 3N NaOH concentrations were the best concentration for NaOH, depending on SEM it is given were irregular, and amorphous, was clearly observed that give high purity nano-silica and high smoothness of the spectrum. It indicates high efficiency to remove impurities.

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