Preparation and Characterization of Nano silica Prepared by Different Precipitation Methods

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Abstract. Agricultural waste Rice husk ash (RHA) is large and massive by the output of rice milling manufacture and contains a high amount of silica. Taking into account this verdant technology is utilized to get SiO2 Nanoparticles from rice shell ash. In this research, studies on the extraction methods of Nano-silica by combustion rice shell for 2 h at 700 °C were carried out and investigated. However, the Rice shell ash was undergoing to precipitation methods and sol gel method to manufacture Nano silica. precipitation methods involve refluxing silica from Rice shell ash in boiled (1.0, 2.0 N NaOH). While the sol-gel method involves calcination of RHA was treated with HCl at 700 °C for 2 h followed by chemical treatment. Results of The Infrared spectral (IR) information display the presence of hydrogen-bonded silanol group and the siloxane groups in silica. The Optical properties through UV-visible spectroscopy of the Nano silica samples show a wide bandgap value and absorption peaks located in the UV region. As well as, the particles size analysis with values of (13.02, 16.83 and 23.96 nm) for the samples (1NSiO2, 2NSiO2, and acid leaching) were obtained respectively.

Keyword: Rice husk waste; Nano-Silica; NaOH; FTIR; UV. Visible
1. Introduction

Nanotechnology attracted much attention of scientists and producers due to the unique physicochemical properties of nanoparticles as compared to their bulk form [Patil et al., 2018]. Nano-sized materials have tremendous potential and used in kinds of industries, like electronics, optical, chemicals, environment, and so on [Nguyen et al., 2012]. Between them, nanosilica is an excessively utilized nanomaterial with applications in adhesives, food additive, sealants, paints, cosmetics, inks, fiber optic strands, polymer, coatings, and in cement-based building materials [Premaratne et al., 2013].

Silica nanoparticles (SNPs) have gained greater attention because of its highly reactive surface area to volume ratio, physical and chemical steadiness, low toxicity, and straight forward surface chemistry [Ghorbani et al., 2015]. There are two forms of Silicate materials amorphous and crystalline. Amorphous silica has large industrial applications. It is utilized in plastics, rubber, electronics, cosmetics, optics, coating, refractories, and also use as an abrasive agent. The crystalline form of Silica is widely utilized in the glass and ceramic industry [Singh et al., 2014]. The properties of Nano-Silica are shown in Table 1.

Table 1: Properties of Nano-Silica [Rao et al., 2016]

| S. No | Characterization             | Actual Analysis       |
|-------|------------------------------|-----------------------|
| 1     | Active Nano Content (%Wt. Wt.) | 30-32                 |
| 2     | pH(20C)                      | 9-10                  |
| 3     | Specific Gravity             | 1.20-1.22             |
| 4     | Texture                      | White Milky Liquid    |
| 5     | Dispersion                   | Water                 |

Tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS) have been usually used as the silica source to produce Nano silica [Shen et al., 2014]. However, these chemical sources are rather expensive and toxic. RHA between the family of agricultural-wastes is the excessive silica-rich, containing silica 90% to 98% and some amount of metallic impurities. [Janasree et al., 2018] The Rice husk is an agro-waste residue that was chosen due to its local very low cost of availability, chemical stability, and its granular structure [Zhang et al., 2010]. The maximum length of rice husk is about 10mm and the width is 1 to 4mm. Due to high calorific value of Rice husk, its utilized to generate electricity [Vinukumar et al., 2016].

In the world, 500 million tons of paddies produce 20% of the Rice husk. Rice husks contain 25% volatile organic matter, with 75% of them turning ash during combustion, called Rice Husk Ash (RHA) [Kim et al., 2014]. Rice husks have been used in many applications, including as a source of energy, where they burn and lead to waste generation. Amorphous silica can be extracted from rice husks at low temperatures [Patel et al., 2017]. White-colored ash is produced If the rice husk is completely combusted. Approximately, every 100 g of rice husk gives 20 g of RHA [Vasamsetti et al., 2018]. After combustion, the organic constituent is decomposed and RHA is gained. [Janasree et al., 2018]. These ashes contain 72.1% SiO2; 0.3% Al2O3; 0.5% Na2O; 0.43% CaO; 0.72% K2O; 0.05% TiO2; 0.15% MnO, 24.3%; 0.06% P2O5 and ~0.7% MgO weight loss on ignition [Dang et al, 2017]. to obtain high purity silica (above 99%) Eliminating these metallic impurities is required by hydrochloric acid leaching of rice husk and then controlled combustion [Bakar et al., 2016]. Rice husk ash is further suitable than rice husk in most applications [Ananthi et al., 2016].
Structural transformation of silica present in the ash occurs depending on the conditions (time and temperature of combustion, metals content, and the chemical composition after combustion). Amorphous ash is formed at 400-1200°C and crystalline ash is formed at a temperature above this [Ananthi et al., 2016]. This product is not suitable for human consumption. The disposal of the ashes and partially boring husk creates environmental hazards. Silica nano production is an inexpensive and important application of rice husk [Kaviyarasu et al., 2016]. There are sundry methods of manufacture Nano silica such as the precipitation method [Premaratne et al., 2013], Sol-Gel method [Rahman et al., 2012], and in situ emulsion polymerization [Moosa et al., 2017]. The main methods of producing silica are [Patel et al.,2017]:

1. Thermal treatment
2. Chemical treatment.

In the present, works involves the extraction of Nano-silica from rice husk by two methods. The first methods involve after thermal treatment, alkaline extraction followed by acid neutralization. While The second method involves the pretreatment of Rice Husk with acid and then thermal treatment. It may be concluded that Nano-silica extracted from rice husk ash can be used for different novel applications.

2. Materials and Methods

Jasmine rice husk was provided by a local rice milling company in Al-Najaf, Iraq. NaOH, Hydrochloric acid (HCL) (35 %, Merck, India) was utilized to eject the minerals impurities from the rice husk. Ethanol and distilled water were utilized wherever needed.

2.1 Preparation of rice husk ash

Firstly, the RH was sieved to remove dust and strange material. Consequently, RH was washed by distilled water several times until its reaching neutral PH value. An electric oven was used to dry the washed rice husk for 7 h at 120°C and then grinding the dried Rice husk by grinder. Followed, the nano-silica was produced by two methods as below:

2.2 Precipitation method

2.2.1 Preparation of sodium silicate solution

Silica was extracted using a method adapting from previous studies with some modification [Patel et al.,2017], [Janasree et al.,2018]. As shown in figure 1 about 50 g of the washed and dried rice husk (RH) was burned in muffles furnace at 700 °C for 2h. The goal of this step is to reduce the material to increase the silica content in the samples, as well as to burn out other undesirable components, and then the solid RHA was blended with 1N Na OH solution in 500 ml Erlenmeyer flask and is allowed to seethe for 2h at 100 °C with constant stirring to dissolve silica. The final mixture was allowed to cool down to room temperature and filtered to separate the filtrate which contains sodium silicate, while the residue was discharged.
Figure 1. Preparation of sodium silicate solution from rice husk

2.2.2 Precipitation of Nano silica

Figure 2 shows the synthesis of Nano silica by precipitation method. Concentrated Hydrochloric acid with regular addition (dropwise) was utilized to reduce the pH of the filter sodium silicate solution while being stirred magnetically. After the stirring period gained pure silica in gel form. An electric furnace at 200°C for 8 h was used to dry the gel. The solids were crushed to powder using the mill, to get the Nano silica particles.

In which the process of synthesis Nano silica by precipitation method display in figure 3 and by the following Eqs. (1 and 2) respectively.

\[
SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \quad (1)
\]

\[
Na_2SiO_3 + HCl \rightarrow SiO_2 + NaCl + H_2O \quad (2)
\]

In this work, RHA was pretreatment by two concentrations of Na OH (1, 2 N Na OH). The silica nanoparticles were left in a vacuum desiccator for more characterization.
Figure 2. Synthesis of Nano Silica by Precipitation Method

Figure 3. Flowchart for preparation of Nano silica by precipitation method [ Janasree et al.,2018]
2.3 Sol gel method

Silica was extracted using a method adapting from previous studies with some modification [Dung et al., 2017], [Rafiee et al., 2012]. As shown in Fig. 4 a 5.0 g of RH was mixed with 1000 mL of 1N HCl for 15 minutes stirring time. and then left in the water bath for 2h at 100 °C to eject mineral ions in RHA. Then, acident-treated RH was purified, washed with filtered water, and then dehydrated at 110°C in the electric furnace. The acident-treated RH was burned in a muffle furnace at 700 °C for 2 h. The gained powder was specified as RHA. in which Fig. 4. show the synthesis process of Nano silica. RHA sample (41.835 g) was mixed with 1000 ml NaOH (2.5 N). The sodium silicate solution was heated in a closed beaker for 2h at 100 with constant whickering. It was then filtered and washed with filtered water. The gained transparent, viscous, and colorless solution was let to cold down to room temperature. Nano silica was synthesis by refluxing of taken away silica with 1NHCl fixed movement at controlled conditions until pH = 7. After the stirring period gained pure silica in gel form. an electric furnace at 200 °C for 8 h was used to dried The gel. The solids were crushed to powder using the mill, to get the Nano silica particles.

Figure 4: Schematic illustration of the synthesis mechanism for Nano silica powder from rice husk ash
3. Characterization Instruments

The prepared silica powder was inspected by FTIR, UV-Visible spectrometer, and particle size analysis. The functional groups of the SiO2 nanoparticles were examined by the FT-IR mechanism in which Nano silica blended with Spectral-grade KBr powder at a weight ratio of 2 mg SiO2: 200 mg KBr in a deep mortar, and then pressed. The blended powder into particles with a thickness and a diameter of (0.5 mm 13 mm), respectively. The infrared (IR) spectrum of Nano silica was measured by using FTIR spectroscopy (FTIR-SHIMADSO, Japan made) through the wavenumber domain from 4000 to 400 cm\(^{-1}\). The optical property was characterized using (T90 Double Beam Spectrophotometer by PG Instruments Ltd) UV-Visible spectrometer for optical absorption at wavelength 200-800 nm. After the powder milled by the mill, the particle size distribution and particle size were examined by using laser particle size analyzer at the Department of Ceramics and Building Materials, Faculty of Materials Engineering, University of Babylon, IRAQ.

4. Results and Discussion

The FTIR spectrum in transmittance mode for (1N SiO\(_2\)) in Figure (5 a) shows peaks at 3456.44, 1641.42, 1425.40, 1103.28, 804.32, and 472.56 cm\(^{-1}\) respectively. The broadband between 1641.42 and 3456.44 cm\(^{-1}\) was because of OH groups and adsorbed water. The preponderant absorbance peak at 1425.40 cm\(^{-1}\) was because of bonds (Si ± O ± Si). The peaks between 1103.28 and 472.56 cm\(^{-1}\) are because of the shaking style of the gel [Patil et al., 2014].

FTIR spectroscopy was utilized to discover the presence of binding groups in the (2N SiO\(_2\)) SNPs (Fig. 6b). The shaking indication concerning 1101.35, 800.46 and 470.63 cm\(^{-1}\) are typical of Si–O–Si bands refer to the asymmetric extension, symmetric extension, and bending, respectively [Ghorbani et al., 2013]. These three crests are the essential index of the SiO\(_2\), which explain the effective manufacture of SNPs. The absorption band for H–O–H bending shaking in water is at about 1635.64 cm\(^{-1}\) [An et al., 2010]. The shade shows broadband about 3450.65cm\(^{-1}\), which is because of adsorbed H\(_2\)O molecules [Rafiee et al., 2012]. There is no peak at about 1825_2800, which means after burning, there are no organic substances. The inorganic metallic ions impurities in RHA were separated into the liquid by HCl leaching RHA suspension. After acid treatment, the organic constituents and silica remained as solid ingredients. The chemical reaction along with the high-temperature calcination for the preparation of Nano silica powder can be described as follows Eqs. (3 and 4) respectively.

\[
100^\circ \text{C} \quad \text{(2h), soaked in water bath } \quad \text{HCl} \quad \text{RHA} \quad \text{MCL + H}_2\text{O} \quad \text{SiO}_2(\text{Ash}) + \quad \text{(3)}
\]

Where M: Na; K; Ca; Fe; Al, Mg…

\[
700^\circ \text{C} \quad \text{(2h)} \quad \text{SiO}_2 \quad \text{(Ash)} \quad \text{SiO}_2 \quad \text{(Nano silica powder)} \quad \text{(4)}
\]

During the high-temperature calcination process, all of the organic constituents were burned out. Finally, white powder Nano silica was obtained (Fig. 5c). FTIR for acid leaching sample the peak at 1101.35 and 800.46 cm\(^{-1}\) because of Si–O–Si asymmetric and symmetric extension style, respectively. The band fixed at 466.77 cm\(^{-1}\) is because of the bending frequency of Si–O–Si. Great broadband about 3452.58 cm\(^{-1}\) refers to the presence of the O – H, extension hesitation to the
Solano series, and the residual adsorbed water. A squad about 1635.64 cm\(^{-1}\) is specific to the bending shaking of H\(_2\)O molecules limited to the silica form. There is no crest at about 2900–3100 cm\(^{-1}\), whose means after burning, there are no organic substances [Rafiee et al., 2012].

**Figure 5.** FTIR spectra of (a) 1N SiO\(_2\) (b) 2N SiO\(_2\) (c) SiO\(_2\) acid leaching (d) All samples within.

Visual properties likewise FT-IR and Raman spectra, UV-Visible are generally susceptible to any nanocrystal surface. Figure 6 shows the UV-Vis spectrum of amorphous silica nanoparticles with Different methods. The strong absorption edge is observed at 200 nm wavelength within all samples. However, another peak in 204 nm presented in 1NSiO\(_2\) and 2NSiO\(_2\) samples were observed [Engku Ali et al., 2017]. The absorption spectra of the prepared samples show a stronger absorption in the UV ray, mention that these samples could be a favorable process for increasing the catalytic activity. As well as, the presence of some other crest which may be because of pollution or because of bi-products this formed during synthesis. The results of UV-visible spectroscopy display absorbance of
synthesized materials in the UV region and shown very low absorbance is in the visible region.

**Figure 6.** UV-Visible absorbance spectra for (a) 1N SiO2 (b) 2NSiO2 (c) SiO2 acid leaching

Figure 7. Reveals the particle size analysis of Nano silica with purity (>95%) [Moosa et al., 2017], prepared by different methods. As can be seen from the chart, the medium size of the particles (1N SiO2) (D50) was 13.02 nm, the medium size of the particles (2N SiO2) (D50) was 16.83 nm and (D50) was 23.96 nm for particles (acid leaching).
Figure 7. The particle size analysis of SiO₂: (a) 1N SiO₂ (b) 2NSiO₂ (3) SiO₂ acid leaching

5. Conclusion

In this research, an experiment work has been made to utilize cheap RHA to production Nano silica by two methods, where found precipitation method give very fine silica particles by using special solvents [Noushad et al., 2012]. And found precipitation method its very easy and efficient methods for Nano silica synthesize and less time-time consuming, as compared with the sol-gel method [Janasree et al.,2018]. in the methods of extraction silica from RHA, in order to gain high purity and amorphous silica which was more favorable in various applications. The acid concentration must be
not minimal than 1 M and The combustion temperature should not more than 700°C [Twej & Shihab, 2018]. FTIR spectra showed the formation of Si-O bond. The got Nano silica could be utilized in a variety of fields and helps to reduce the concerns of RHA disposal [Anh Tuan et al., 2017].

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