Evaluation of acid leaching process and calcination temperature on the silica extraction efficiency from the sustainable sources

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Abstract. In the present work, amorphous silica (SiO\textsubscript{2}) is prepared from agricultural waste (rice husks) as a sustainable source by acid leaching process followed with the calcination process. RH treated with 3N HCl then burned at (500, 600, 700, and 800°C) for 4 hrs. The final product of silica was characterized by X-ray fluorescence (XRF), scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, and thermogravimetric analysis (TGA). The results by XRD and XRF indicate that the obtained white powder was amorphous silica at calcination temperature less than 700°C with a purity of 96.976% but at 800°C the purity was 96.983%. SEM and visual inspection analyses show that RHA morphologies with acid pre-treatment at 700°C and 800°C surfaces of un-leached rice husk have a greater degree of roughness than those that have been leached with dilute acids.

Keywords: Rice Husk Ash (RHA), Amorphous Silica (SiO\textsubscript{2}), Leaching Process, Rice Husk (RH), Pre-treatment.

1. Introduction

Rice husk (RH) is one of most important types of natural agricultural waste that contains more than 70% of silica by mass. Other metallic elements are included in the RH-like potassium, sodium, magnesium, and calcium [1]. Amorphous silica has unique properties that make it in a wide range used in many applications, such as silica gels, plastics zeolites, catalysts, ceramics synthesis, silica chip, capacitor/energy storage, activated carbon, and ingredients for lithium-batteries [2-14]. Silica is generally found in the earth’s crust that exhibits either crystalline or amorphous structure. RH is generated during the rice milling process as a by-product [3]. The major inorganic component of the rice husk is silica [15]. The world harvest of rice is estimated at 600 million tons per year [6]. The husk is considered as 20% of the weight grain, through the combustion of the husk, converted 20% of the husk to ash (RHA). Usually, Rice husk (RH) and rice husk ash (RHA) usually remain as unused agricultural waste and cause significant environmental pollution. As a result, a large number of potential industrial applications of silica extracted from RH have been investigated. Also, using cheap resource materials like rice husk to produce important material as nano-silica produces huge economic benefits due to the reduction of the cost and utilization of the waste. The preparation process, properties, and applications of RHA are studied by extensive researches during the last three decades [15-19]. Weiting Xu et al. [20], produced silica from highly reactive biomass (RH) in a new and environmentally friendly way using pre-treatment water. They have found that potassium is the main polluted mineral that stimulates the formation of unwanted black carbon particles and low crystallization temperature for amorphous RHA silica.
Pre-boiling water and acid etching treatment on RHs significantly removes mineral impurities and reduces the sensitivity of RHA crystallization to the calcination temperature. Nittayuthuadaij et al. [21], prepared nano-silica by precipitation method and characterized by many analytical techniques. They found that the obtained product was amorphous nano-silica and the specific surface area was 656 m²g⁻¹. The purpose of the present work is to produce amorphous silica from Iraqi RH by thermal reduction process and to study the parameters that effect on purification process and calcination.

2. Experimental work

2.1. Materials

The raw RH was obtained from Al-Najaf city, Iraq. Chemicals used in pre-treatment is hydrochloric acid (35%) obtained from Merck, India. Table 1 shows RH composition.

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

2.2. Pretreatment of rice husk

The raw RH was separated from dirt, clay, and dust. In the first step, the contaminants were removed by washed with water. After that, it was dried for one day under sunlight, then started acid leaching for 100g of raw materials (rice husk). It is refluxed with an acidic solution carried out in 500 mL of 3 N HCl for 4 hrs at 80°C under stirrer in a glass beaker with a mechanical mixer. After the acid leaching process, it was washed by distilled water to remove the acid. It was dried in the oven upon 100°C until 6 hrs. The experimental set-up for the leaching process is shown in Figure 1. The rice husk with pre-treatment is designated as (RH').

![Image](image1.png)

Figure 1. a) Rice husk (RH), b) Leaching experiment set-up, c) Rice husk with pretreatment (RH').

2.3. Calcination treatment

A sample of 100 g from agricultural wastes (RH) is calcinated (pyrolysed) at temperatures of 500, 600, 700, and 800°C. The pyrolysis process is achieved in a furnace (Lenton furnace, UK) for 4 hrs and the rate of heating was 10°C/min. An obtained powder is designated as (RHA).

3. Results and discussion

Chemical treatment with 3N HCl affected the color of RH from the basic yellow color of the spike to brown, the changes of color during thermal and chemical treatment is also notable. The RH was burned at different temperatures after washing with hydrochloric acid. RH is burned in the furnace, mostly combustible materials can be burned and left some solid products, in this case called RHA, inorganic components, especially silica, were obtained as a solid component.
At 500°C, the color of RHA powder was a little grey due to high carbon content. The color of RHA at 600°C is pinkish-white color ash observed, which means the total conversion of RHA to amorphous silica. The color of RHA with treatment at 700°C is higher whiter than RHA without treatment at 700°C. Also, RHA at 800°C has appeared as a very white powder and with pre-treatment was a bright white powder, as shown in Figure 2. Rising the temperatures to 500, 600, 700, and 800°C leads to dissociation of metal oxides and that reducing the black particles. The highest percentage of potassium oxide K$_2$O is the reason why ash has grey color instead of white. The temperature has a significant effect on the content of carbon. Increasing the temperature to K$_2$O decomposition point lead to melt the unburned carbon. So, carbon is surrounded by the molten thus the air cannot reach to it and that causes incompletely burned of carbon. Even at high burning temperatures, the potassium oxide from RH does not volatilize if the RH is untreated before burning. The chemical treatment with HCl is very important for reducing metal oxides and increasing the purity of produced RHA and that leads to raising the degree of whiteness for the produced RHA. Figure 2 shows that the ash structure of RH can be extracted at different calcification temperatures.

![Figure 2. RHA without pretreatment heated at, (a) 700°C, (b) 800°C. RHA with pretreatment heated at, (c) 700°C, (d) 800°C.](image)

Table 2 illustrates the characterization of RHA, which found that rice husk with 3N HCl removed most of the organic components. Ash resulting from the complete combustion of RH treated with acids was very white then untreated RH at same conditions.

| Chemical treatment       | Thermal treatment (°C) | Observation                      |
|-------------------------|------------------------|----------------------------------|
| Without chemical treatment | 500 °C for 4hrs.       | Coarse powder, incomplete combustion, slightly grey |
| Without chemical treatment | 600 °C for 4hrs.       | Fine, pinkish white              |
| Without chemical treatment | 700 °C for 4hrs.       | Fine, white                      |
| Without chemical treatment | 800 °C for 4hrs.       | Fine, pure white                 |
| Chemical treatment, 3N HCl | 500 °C for 4hrs.       | Coarse powder, white             |
| Chemical treatment, 3N HCl | 600 °C for 4hrs.       | Fine, white                      |
| Chemical treatment, 3N HCl | 700 °C for 4hrs.       | Fine, pure white                 |
| Chemical treatment, 3N HCl | 800 °C for 4hrs.       | Fine, pure white                 |

Conditions for the conversion process such as pretreatment and the temperature of combustion determine the end products properties. The purity of prepared silica from RH was measured by X-ray fluorescence (EDX-7000, Shimadzu/ Germany). Table 3 reveals the XRF analysis of the chemical composition for RHA.A notable vary in chemical composition of Iraqi RHA with and without acid treatment at different burning temperatures as shown in table 3. The main component of RHA, which is created at moderate combustion temperatures is amorphous SiO$_2$ in the range of purity 84-97%.
The reaction of silica production can be described together with the process of calcination at different temperatures as:

$$\text{SiO}_2 (\text{colloidal RH}) \rightarrow \text{SiO}_2 (\text{RHA particle})$$  \hspace{1cm} (1)

Table 3 reveals that the acid treatment reduces the amount of carbon content because of impurities dissolution.

Table 3. XRF analysis for RHA with calcination at different temperature for 4hrs.

| Component | 500°C | 600°C | 700°C | 800°C |
|-----------|-------|-------|-------|-------|
|           | without pretreatment | with pretreatment | without pretreatment | with pretreatment | without pretreatment | with pretreatment | without pretreatment | with pretreatment | without pretreatment | with pretreatment |
| SiO₂      | 84.639 | 86.361 | 91.489 | 94.432 | 92.437 | 96.976 | 92.579 | 96.983 |
| CaO       | 4.387  | 3.615  | 3.101  | 1.103  | 1.374  | 1.482  | 1.103  | 1.046  |
| Fe₂O₃     | 2.216  | 2.072  | 1.604  | 0.763  | 1.513  | 0.467  | 1.163  | 0.415  |
| K₂O       | 5.131  | 4.385  | 3.079  | 1.862  | 1.733  | 1.011  | 1.462  | 1.133  |
| Cr₂O₃     | 0.741  | 0.728  | 0.065  | 0.043  | 0.044  | 0.025  | 0.023  | 0.012  |
| S₂O      | 0.887  | 0.341  | 0.117  | 0.084  | 0.052  | 0.001  | 0.001  | ---    |
| MnO       | 1.161  | 1.082  | 0.160  | 0.093  | 0.013  | 0.022  | 0.007  | 0.013  |
| other     | 5.477  | 4.161  | 3.850  | 1.620  | 2.834  | 0.016  | 3.663  | 0.398  |

Also, increasing combustion temperatures from 500°C to 800°C has raised the purity of the silica content. Increasing amorphous silicon oxide content is connected with rising the temperature of combustion. The optimum concentration of silica was obtained with concentrations 3N of HCl and the silica reached up to (96.976%) at 700°C. The combustion temperatures were not effective without chemical treatment for RH with a purity of silica reached to (92.437%). On the other hand, the thermal treatment is effective in diminishing the carbon materials. Also, the volatiles is probably carried out from the RH during thermal decomposition.

3.1. Thermogravimetric analysis (TGA)

Chemical composition of RH generally consists of ash (silica and other impurities), organic constituents (lignin, cellulose, and hemicellulose) with moisture. The thermal decomposition of RH was depended on the constituent’s decomposition behaviors. Thermogravimetric analysis can quantify the major contents besides observe the thermal behavior alterations in samples. The TGA determines the thermal behaviors of untreated and pretreatment rice husks as revealed in Figure 3-a, b respectively.

Figure 3. Thermogravimetric analysis (TGA) curves for, a) untreated RH, b) pretreat RH with 3N HCl.

From Figure 3, it can be noted that the thermal stability of treated RH is more than untreated RH. The acid hydrolysis of organic materials in pre-treated RH causes reducing in the molecular weights compounds comparing with un-leached rice husk and that makes it easily thermo-degraded.
TGA revealed the mass loss in rice husk at three stages. The first stage is moisture removing, the second stage is releasing the volatile matter and the third stage is a combustion of the combustible material. In untreated RH, the first losing in weight occurred at 50–150°C, as approximately 1–2.5% which was corresponded to loss due to the vaporization of physically adsorbed water and removal of moisture. The untreated RH releases the volatile matter at the range 150–298.8°C caused losing weight at the range of 9.8%. Also, treated RH releases volatile matters at the range 145–306.7°C. Rising the temperature to almost 300°C caused losing weight at the range of 16.6%. At 300°C till 600°C, the RH starts decaying with 75 wt.% weight loss, involving decomposition of secondary volatile products, such as different forms of cellulose, hemicelluloses, and lignin. In the temperature range of 150-500°C, cellulose, hemicellulose, and lignin were decomposed thermo-chemically. Hemicellulose was decomposed mostly between 150 and 350°C. The reduction of RH weight begins to occur at 250°C strong and completes at around 380°C, the reduction was 56.8153% of weight loss causes as shown in Figure 3-b. The decomposition of cellulose occurs between 275 and 370°C while the lignin affords gradual decomposition between 250 and 600°C. This weight-loss attributes to convert the lignin to char and also to burn the residues of carbonaceous as ash product. The range above 600°C, the low mass 24–26% may be carbon combustion which is adsorbed on the surface of the solid material to result the residual ash (white silica powder).Residual ash is usually the noncombustible silica ~20-26%, >500°C. The separation of rice husk components degradation is not possible because of the superposition of the degradation process and reaction complexity. The examination results show that the thermo-gravimetric curves decreased with increasing temperature. This is due to the carbonization and de-carbonation of RHA. Carbonization is the decomposition of RH at temperatures greater than 300°C. De-carbonation is the calcination of the carbon in the rice husk at higher temperatures in the presence of oxygen.

3.2. Morphology analysis by (SEM) of RHA
The morphological features of the RHA at 700°C, observed by scanning electron microscopy (SEM) (Vega3, TESCAN, USA) are shown in Figure 4.

Figure 4. Scanning electron micrograph (SEM) micrograph of RHA at different scale morphologies.

Figure 4-a,b, and c, offer RHA outer surface at different scale morphologies, the images show RHA outer surface is uneven with high roughness and also an epidermis of RHA became loose, lumpy, and rugged. Silica in RHA is ubiquitous but concentrates on the hair at the outer epidermis, protuberances, and adjacent to the rice nucleus. Silica particles clearly appear RH outer surface is uneven and very rough. The structure of the organic content in RH has suggested the bonding way between Si and organic materials. RH partial burning caused decaying the organic molecules and bonds shatter with Si. Figure 5 shows the outer surface morphology of washed acidic rice husks. RH morphology appears important change after leaching with acid. The results showed that the surfaces of untreated RH possess high roughness more than the sample washed with dilute acids, it is clear that the outer surfaces are smooth after leaching the acids. This is likely because the acids effective of hydrolysis the organic materials as shown in Figure 5 and 6.
Figure 5. Scanning electron micrograph of RHA with pretreatment by 3N HCl at burn temperature 700°C.

Stripping occurs in rice husks by the combustion process of carbon and volatiles RH internal surface shows up clearly and RH external surface is partially taken off as shown in Figure 6.

Figure 6. Honeycomb morphology by (SEM) of RHA at different magnifications at burn temperature 700°C.

RH structure between internal and external layers has a loose mesh of pores with pieces of crossed plate. The absorbed surface porous structure shows the RH structure. So that, the pores are easily seen via SEM, and it is named network honeycomb or RH structure. Figure 6-a, and b, shows the porous and honeycomb morphology which can be related to the burning of the organic component in the rice husk during combustion. Aqueous silica is subsequently polymerized to form a network of skeletal silica that may explain the scaly and honeycomb-like structure in an SEM microscope, Figure 6-c. It shows small forms of the RHA sample that contain multiple vertical and horizontal overlapping sheets. Also, little grainy pieces of RHA sheet are noted. Cell walls around the follicles are broken and stretched upon heating, and the arranged retinal backbone is somewhat exposed due to the combustion of less dense materials.

3.3. XRD for RHA

According to our experimental work on burning the rice husk at different temperatures and with the chemical treatment that gives silica with a high degree of purity.
The burning of the RH at a temperature below 700°C produces an amorphous structure of silica but when the temperature increases to 800°C the silica will be transformed to alpha quartz, as shown in Figure 7. The Figure 7-a to d, shows the characteristic feature of amorphous silica which is a broad smooth hump located between 15° and 31° (2θ). That indicates the pyrolysis at a temperature less than 800°C will transform the RH structure into a disorganized amorphous structure that can be able to adsorb. Increasing the temperature to 700 °C leads to a slight rising in the density of peak in (2θ) 22°. At 800°C, the intensity of peak much increased in (2θ) 22°. Additionally, other peaks have shifted to lower and higher 2θ values and observed at 34°, 45°, 47° and 49° (2θ), according to (JCPDS-card #96-900-1582) in (JCPDS) Standards Joint Committee on Powder Diffraction. To show the effect of high combustion temperature on silica, in Figure 7-d show prepared the sample at 800°C.

![Figure 7.XRD of pretreatment RHA, at a) 500°C b) 600°C c) 700°C d) 800°C for 4hrs.](image)

At this temperature, besides the amorphous peaks, some sharp diffraction peaks were clearly exhibited silica. This indicates that some crystallites have been formed at 800°C in the RH combustion. The burning out temperature is a very important factor to define whether the silica stills amorphous or become crystalline. Overall, the structure and properties of silica derived from agricultural waste are strongly influenced by the extraction method used [22]. Morphologies obtained from either amorphous silica or crystals depend on the temperature or chemical treatment. The quantitative crystalline ratio can be calculated from (XRD) as observed in table 4. It is shown amorphous content lower to 58.44% at a combustion temperature of 800°C, while crystalline content was higher 41.56%. This give indicates that an increase in combustion temperature upper then 800°C will form crystalline particles and with nanoparticle size.

| Temperature, (°C) | Degree of Crystalline content (DOC) |
|------------------|-------------------------------------|
| 800              | 41.56                               |

Table 4. Quantitative crystalline ratio at 800°C for silica.

4. Conclusions

The silica from RHA material was successfully synthesized from the abundant Iraqi rice husk. The initial washing of the RH with HCl solution was carried out before combustion. It was found that
pre-treatment is necessary to obtain relatively pure silica (96%). Acid treatment with 3N HCl treatments followed by the calcination process at the burning temperature of (700°C) was the best for the production of highly pure amorphous silica. Also, calcination temperature and acid treatment with 3N HCl has a significant effect on the morphological features of RHA. The RHA at 800°C appeared as a very fine and white powder.

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