Nanoparticles Extraction from Rice Husk Ash: A review

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Abstract: Rice is the staple food of many countries, especially in the Asia region which holds the highest consumption of rice with 90% globally. Rice husk is a solid agricultural waste of rice milling which needs a proper waste management. Rice Husk are a renewable resource which is widely used to extract nanoparticles for various applications. One such type of nanoparticles which are extracted from rice husk is the silica particles. In order to extract these silica particles various methods and procedures are used. In this review it gives a detailed explanation on how the silica particles are extracted from Rice Husk by various methods of extraction. It also highlights the applications of these extracted nanoparticles and the properties of Rice Husk Ash. Two main methods discussed for the silica extraction are the physical and the chemical method. Additionally, it also highlights the other methods which are used for the process of extraction of silica particles from Rice Husk.

Keywords: Rice Husk, Silica, Rice Husk Ash, Milling, Nanoparticles

1. Introduction

Globally, India is the second largest producer of paddy after China in the world. In India approximately 20 million tons of paddy is produced, giving 24 million tons of Rice Husk and 4.4 million of tons of Rice Husk Ash every year, producing a huge amount of solid waste. Paddy consists of 20-22% of rice husk. Rice Husk has a high calorific value of 2938.86kcal/kg. It is the cheapest and the most common renewable energy source, however by burning of Rice Husk it becomes hazardous for the environment as well our health if it not being disposed properly. Burning of Rice Husk converts the organic components present into 20% carbon dioxide, air and ash Rice Husk has a high silica content and it does not burn with an open flame or decompose completely. The concentration of silica in Rice Husk Ash is influenced by the fluctuations of geographical and environmental conditions, including factors such as climate, harvesting seasons, soil composition and the quantity of fertilizer used in the cultivation. The dry Rice Husk contains of 70-85% organic matter such as lignin, cellulose and hemicellulose which makes it suitable for use in feedstock in bioethanol. From the 70-85%, 21.44% of lignin, 32.24% cellulose, 21.34% of hemicellulose and the inorganic remainder 20-25% which mainly consist of silica. Silicon Dioxide (Sio2) or silica, exists in two forms, amorphous and crystalline. Naturally silica is rice husk ash is amorphous, however when combustion above 650ºC the silica changes its phase from amorphous to crystalline. Silica in amorphous state has a large surface area and is a high purity than crystalline silica which comes under the IARC Group 1 carcinogenic agent. Amorphous silica is known for its wide range of industrial applications, such as coatings, plastics, rubber, electronics, abrasives, refractories and optics. It also serves as a pivotal precursor for synthesis of wide range of fine compounds. These include sodium silicate, zeolite catalysts, aerogels, and ultrapure silicon. As Rice Husk is a renewable energy source and silica can be extracted from this renewable energy source, there has been a lot of interest in developing efficient and

sustainable methods for extracting silica from rice husk. The most common methods are physical and the chemical method. In chemical method, different procedures are used. Additional methods which are used to extract nanoparticles from rice husk includes: Hydrothermal, Precipitation and Technical grade solvent.

2. Silica in rice husk

Silica exists in two primary forms, which is the amorphous and the crystalline forms, however it is also in gel form. Silicon Dioxide or silica (SiO2) is an important inorganic multipurpose chemical compound. From the extracted silica there are number of specialized silicas produced which are used for various applications. These specialized silicas include colloidal silica, fumed silica, fused silica, high-purity ground silica, silica gel and precipitate silica. The increasing need for these particular silicas has resulted in significant yearly income surpassing $2.5 billion, driven by a steady 3% annual expansion. Remarkably, the greatest utilization of specialized silicas is currently seen in the Asia Pacific Area, with the demand reaching $800 million in 2003.

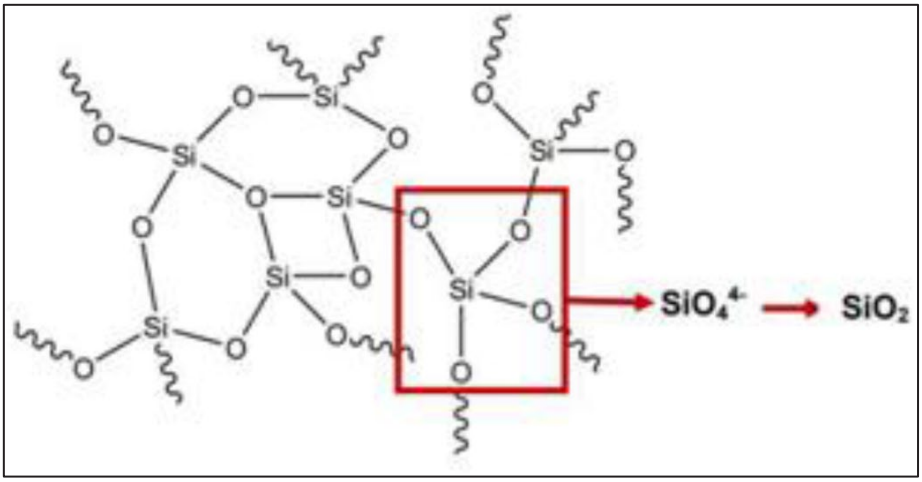

Fig.1. The structure of silica

Due to the classification as an IARC Group 1 crystalline silica is a carcinogenic agent, which makes this silica form hazardous to human with potential health risks. In 2010 the Occupational Safety and Health Administration (OSHA) issued a risk assessment regarding occupational exposure to respirable crystalline, with a limit of 0.05mb/m. OSHA used the “Life Table Method" to estimate the excess cancer risk associated with various levels of crystalline silica exposure based on seven published hazard function estimates. Due to its carcinogenic behaviour, there has been explorations for alternative silica sources which are not harmful and hazardous for human. These alternative forms of silica include amorphous ground silica and fumed silica. In the crystalline form of silica there are two types of polymorphs found depending on the combustion conditions. These two types are quartz and cristobalite. Quartz (α-SiO2) is abundant in nature and has a hexagonal crystal structure with a bonding structure of silicon-oxygen (Si-o). Cristobalite exists in two forms, β-cristobalite and α-cristobalite with a tetrahedral arrangement of silicon and oxygen. Amorphous silica has a high purity compared to its crystalline form. This type of silica differs from crystalline structures due to its disordered atomic arrangement, lacking the long-range order found in crystals. It is abundant in RHA (rice husk ash) and stands apart from crystalline forms like quartz and cristobalite. Its unique properties make it valuable for various industrial and research purposes. Amorphous silica is used in adhesives, plastics, rubbers, electronics,

optics, fire-retardant materials. Additionally, it is also used in the production of chemicals such as sodium silicate, zeolite catalyst, aerogel, highly pure silicon, silicon nitride and silicon carbide. Industries like biotechnology and pharmaceutics has a high demand for amorphous silica because of its excellent unique properties.

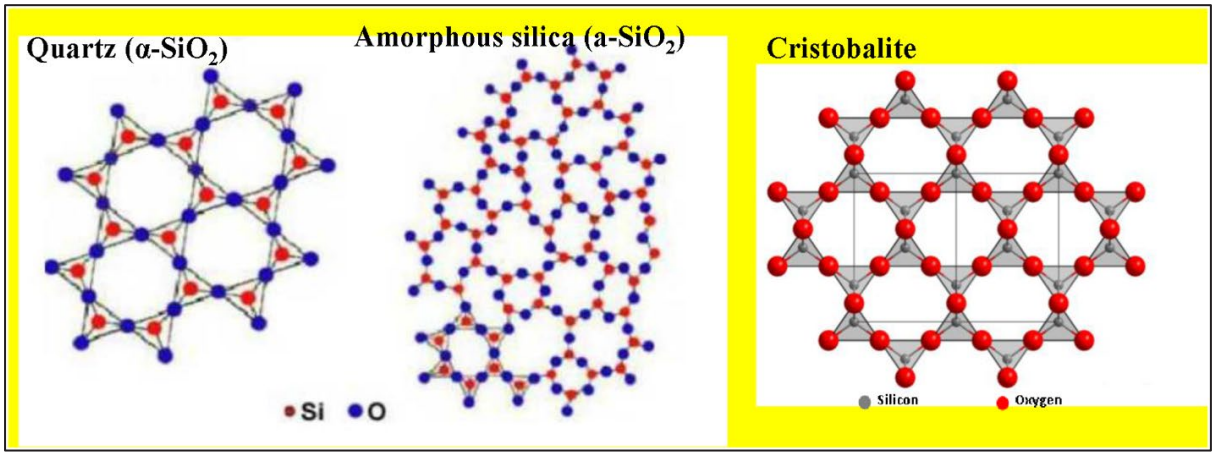

Fig.2. Different forms of silica

METHODS OF NANOPARTICLE (Silica) EXTRACTION FROM RICE HUSK ASH:

There is an increasingly high demand for silica in various industries, due to its unique properties and its abundant nature only from one source which is the rice husk. The original source being the rice husk however in different methodologies different forms of rice husk will be used, which mostly is the rice husk in the form of ash. The two main methodologies which are used in order to extract nanoparticles from rice husk are the physical and the chemical method, in which there are various chemical methods. Apart from these two methods it includes Hydrothermal, Precipitation and use of technical grade solvent.

2.1 PHYSICAL METHOD (DIRECT THERMAL COMBUSTION):

One of the ways to extract silica from rice husk is the direct thermal combustion method. The rice husk undergoes direct thermal combustion, which then becomes Rice husk ash (RHA). These rice husk ash contains 85-95% of silica content in it after the direct thermal combustion. The two main ways in which the silica is extracted from thermal combustion are from calcination and pyrolysis followed by acid leaching

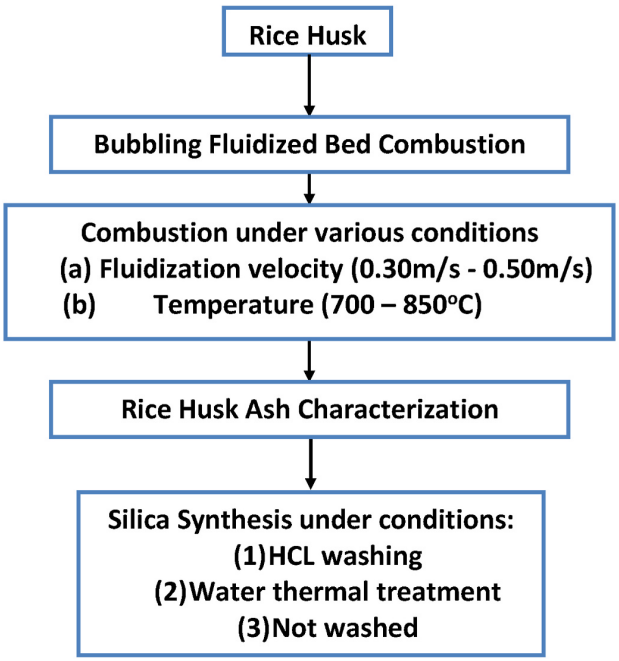

Fig.3. Process of direct thermal combustion

This process is a two-stage continuous process, combining the direct combustion and acid leaching. First is the production of rice husk ash by feeding he rice husk in to the reactor at a temperature of 600 ◦C. The temperature is maintained at 600 ◦C in order to prevent the rice husk from forming crystalline silica. This process forms two products: rice husk ash and flue gas at a percentage of 90% and 10%. The second step is acid leaching. The rice husk ash undergoes acid leaching with Hydrochloric acid and water at a ratio of 1:3:6. It is observed that the direct combustion in a continuous reactor is efficient and stable producing RHA with high silica content and low crystallinity. Then the properties of RHA after acid leaching process were analysed. The RHA demonstrated a surface area of 19.5 m2 /g, a pore volume of 0.06 cm3 /g, and a pore size of 12.4 nm. On the other hand, the silica exhibited a surface area of 226.7 m2 /g, a pore volume of 0.36 cm3 /g, and a pore size of 6.4 nm, in addition to high purity (99.9 %) and low crystallinity (1.8 %) Thermal energy and steam are generated in this process, which further is used for Power generation At a range of 550-750 ◦C amorphous silica is formed and at a temperature range of 800-1000 ◦C crystalline silica is formed. In this process maintaining a constant temperature is very important, because if the temperature goes beyond 750◦C crystalline silica will be formed, this should not be the outcome rather it needs to form amorphous silica. A phase shift towards the tridymite and cristobalite once the temperature starts reaching 600◦C. As the temperature of the combustion rises, the characteristics of silica also experience alterations. From a study conducted by soltani et al it was found that higher combustion temperatures result in larger ash particle sizes and a reduction in the presence of meso and micropores. The factors affecting the combustion or the success parameters of amorphous silica extraction includes these factors:

- Temperature Control
- Rice Husk Characteristics
- Residence Time
- Oxygen Availability
- Cooling Rate
- Surface Area and Purity

- Precursor Treatment
- Instrumentation and Monitoring

The above mentioned parameters play a huge role in achieving the desired amorphous silica structure from RHA. It is extremely important to control these factors for a successful production of amorphous silica, which has a high demand in various industries.

2.2 CHEMICAL METHODS:

Even if the combustion process is a direct method of Nano-silica extraction, the method has some drawbacks. One such is that when the RHA is left untreated with acid or alkali, it weighs less than 95% of silica, remaining goes to impurities. However, when the RHA is treated with an acid or an alkali the weight of Sio2 increases to 99%. This result in exploring various methods to extract nanoparticles using chemical methods. Amorphous silica is highly soluble with a PH of 9.14. There two types of chemical methods: acidic and alkaline, which method to be used is dependent on the PH of the chemical to be used in the process.

2.2.1 Alkaline methods:

Using technical grade solvent Silica has a PH level of 9.14 and goes beyond 10, which makes it easily soluble and therefore the extraction is carried out using alkaline solvents. In this method the extraction is carried out by adapting the method of Kalapathy and Handyman. 25 g of the RHA was mixed with 0.50 N, 0.75 N, and 1 N NaOH solution in the various ratio: 1:4, 1:5 and 1:6. The mixture was the heated at 80°C with constant stirring for one hour in order to dissolve the silica and produce a sodium silicate solution. Solutions were filtered through Whatman no. 41 ash less filter paper. The filtrate was allowed to cool to room temperature and titrated with 1 N HCl with constant stirring to pH 7. The silica gels formed were aged for 24 hours. Distilled water was added to gels and then the gels were broken to make slurry. Slurries were then washed repeatedly (4 times). The gels were transferred into a beaker and dried at 70°C for 22 hours to produce xerogels. The composition of minerals in RHA is shown in the fig 4. The gross weight of Silicon dioxide (Si02) in the RHA was 73.85% and others were residual. RHA was produced by burning at 600°C to produce amorphous silica. However, in this process obtained a yield of RHA only 21.14%. The combustion changed rice husk became silicon dioxide followed the chemical reaction below.

C, H, Si, O2 □□CO2 (g) + H2O (g) + SiO2 (s)

Composition	Value (%)
SiO_2	73.85
Na_2O	0.07
K_2O	2.78
CaO	0.61
MgO	0.64
Fe_2O_3	0.40
Cl	0.29
Al2O3	0.53
MnO2	0.14
P2O5	1.72

Fig.4. The composition of rice husk ash

2.2.2 Using Ballmill and Coprecipitation

This is another method in which comes under the alkaline methods. The extracted RHA from this method can be used further as a filler in Nano composites. FTIR, SEM and XRD characterization has also been obtained. (a) Represents Ballmill and (b) represents precipitation.

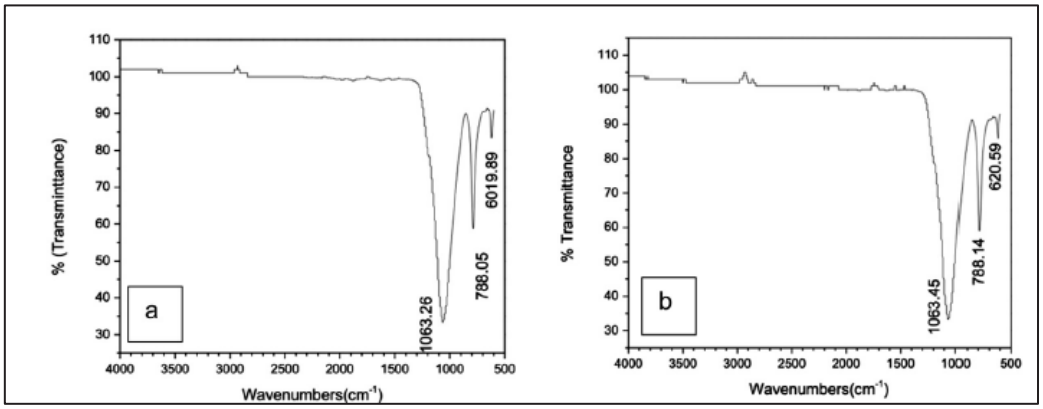

Fig.5. FTIR Characterization of RHA

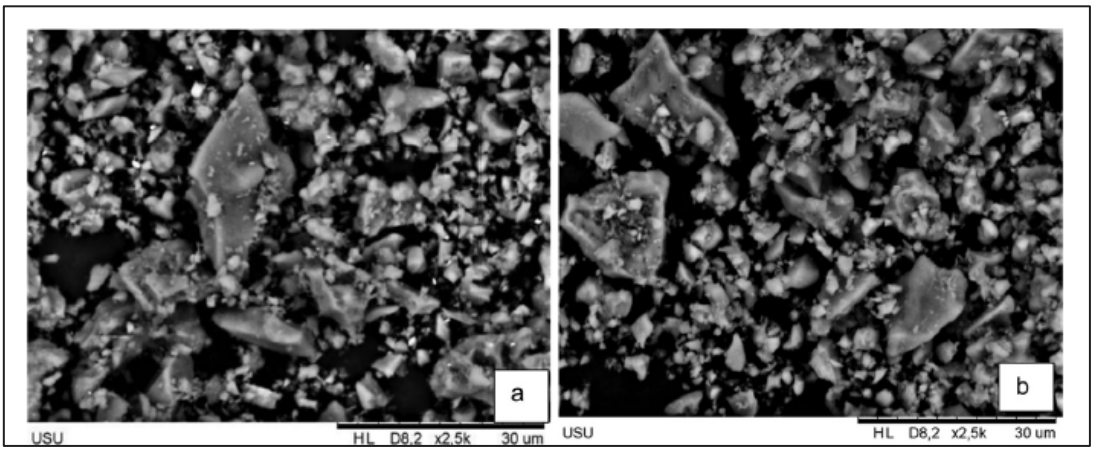

Fig.6. SEM Characterization of RHA

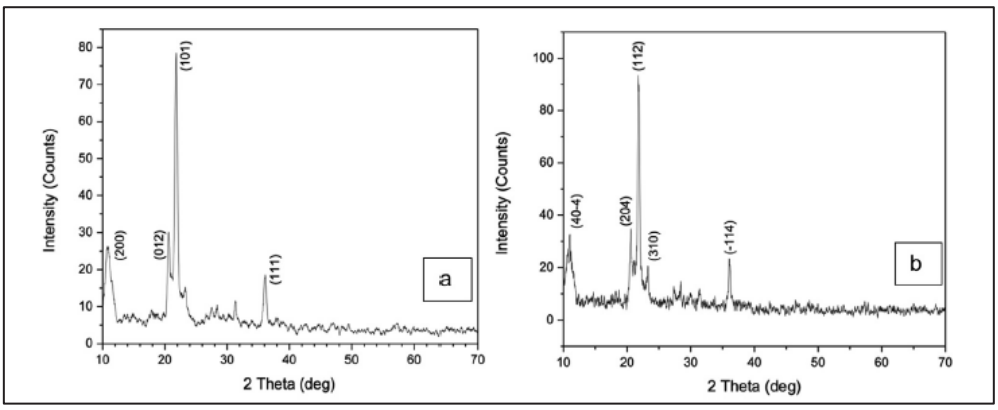

Fig.7. XRD Characterization of RHA

Raw RHA obtained from rice processing was claimed at a temperature of 500 °C for 5 hours and the milling for 10 hours with a rotation of 250 rpm. Furthermore, RHA was mixed with 5 M HCl in a ratio of 1:4, stirred, and heated with a magnetic stirrer at 70 °C for 4 hours at a speed of 400 rpm. RHA, which has been mixed with 5M HCL, is filtered using filter paper, then remixed with NH4OH in a ratio of 1:4, stirred, and heated with a Magnetic Stirrer at a temperature of 70 °C for 4 hours at a speed of 400 rpm. Then filtered and washed with distilled water to produce a neutral pH and dried in an oven at 150 °C for 5 hours.

Precipitation Method: In this method the solution used are sodium hydroxide powder (NaOH), hydrochloric acid (37%HCL), sulphuric acid (98% H2SO4). The collected Rice Husk has been washed thoroughly with distilled water to remove rice grains, sand, and other heavy impurities. It is 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 produce Rice Husk Ash (RHA), the ash was collected and milled to get fine particles.

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 colour which indicates the absence of carbon atoms and obtains pure white silica powder.

Fig.8. 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 sulphuric acid (H2SO4) were added with continuous stirring until the pH reached between 4-3.5 and silica gel was formed.

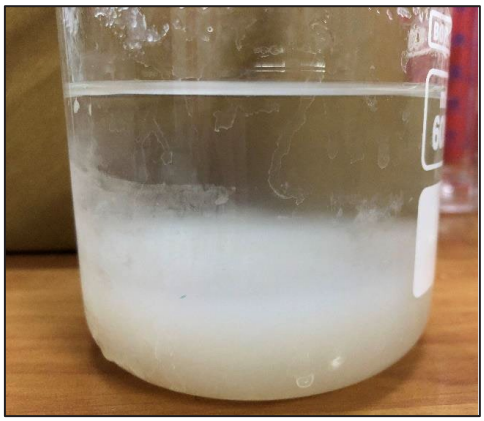

Fig.9. Silica gel

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 nanoparticles.

2.2.3 Hydrothermal process

The Hydrothermal process comprises three primary stages: alkaline treatment, acid leaching and filtration. During alkaline treatment, rice husk is mixed with sodium hydroxide (NaOH) or potassium hydroxide (KOH), then heated at 80-100°C for several hours. This process dissolves the lignin and hemicellulose in the rice husk, leaving behind the silica-rice ash. Acid leaching involves adding hydrochloric acid (HCL) to the ash and heating 80-100°C for several hours to remove metal impurities and enhance the silica purity. Filtration separates the silica from liquid phase using filter paper or a membrane. The extracted silica typically exhibits high purity levels ranging from 83% to97% depending on process conditions and parameters. The silica has a high surface area, porosity and reactivity.

2.2.4 Acidic Method: Rice Husk can undergo acid treatment either prior to or following the combustion process in order to remove organic materials and metallic contaminants. When the acid treatment is conducted post-combustion to extract silica from RHA, the process is referred as acid extraction. One of the acid treatment processes is known as the Taguchi method.

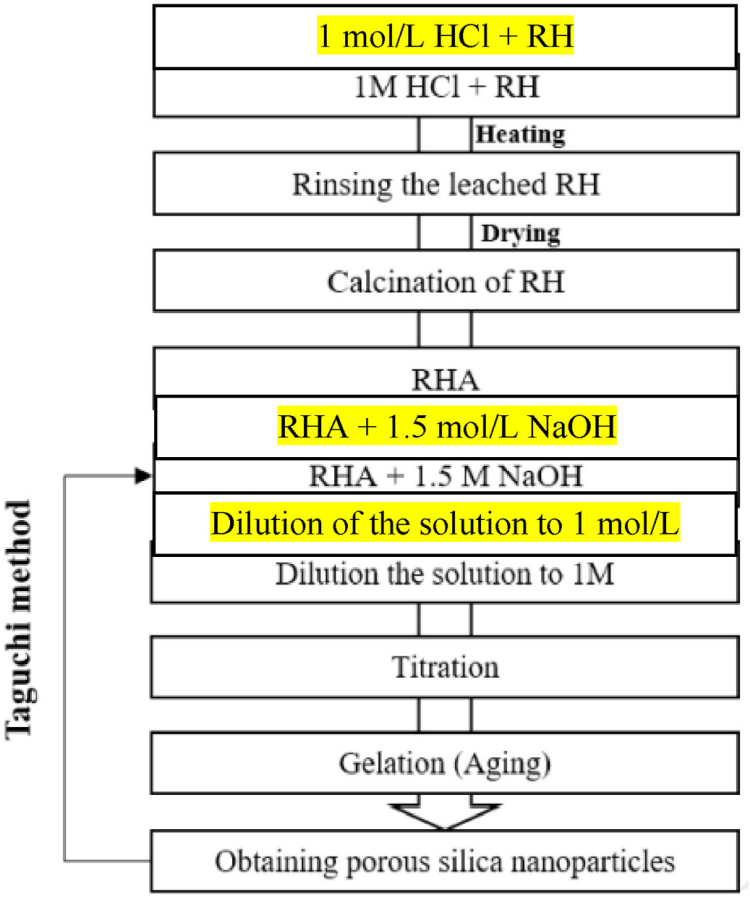

Fig.10. Flowchart of Taguchi method

2.2.5 Applications of extracted silica:

The unique properties and sustainable sourcing of silica derived from rice husk have sparked significant interest across multiple industries. Rice husk, an abundant agricultural by-product which also contains a high silica content. From agriculture and construction to electronics and renewable energy the use of rice husk derived silica is creating new innovations and sustainable advancements. A wide range of applications of silica are listed below.

- Application in ceramics and glass industries: Silica is used in the production of refractory insulating materials, white ceramics, and various oxide ceramics like mullite and cordierite. In glass industries silica is used as a refining agent in order to eliminate the impurities.
- Application in plastic and rubber industries: Silica acts as a reinforcing filler, which results in improvement of tensile, flexural modulus and hardness and mechanical properties. It also reduces the material cost of plastic and rubber products.
- Application in catalyst: RHA derived catalysts have been implemented in various reactions, such as esterification, trans esterification for biodiesel production.
- Energy storage: In lithium-ion batteries and in anodes.
- Construction materials: Substituting some cement with RHA makes construction more sustainable without compromising and improving concrete performance.
- Synthesis of specialized materials: One of specialized applications is the synthesis of mesoporous materials, such as MCM-41. Another specialized material from silica includes Opal.

3. Conclusion

In conclusion, rice husk, a by-product of riced milling, offers a sustainable source of silica, which has diverse applications across industries. With India being a significant producer of rice, the abundance of rice husk underscores its potential as a renewable resource. Extracting silica from rice husk presents an opportunity to mitigate waste while meeting the demand for silica in various sectors. The extraction methods discussed, including physical and chemical processes, highlight the versatility and potential of rice husk-derived silica. From ceramics and construction to energy storage and catalysts, the applications of silica derived from rice husk are numerous and promising. As industries continue to explore sustainable alternatives, rice husk-derived silica stands out as a valuable resource for driving innovation and sustainability.

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