Clean and Efficient Synthesis of High-Quality Silica From Rice Husk Ash

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Abstract

Rice husk ash derived from the rice husk, a renewable waste biomass resource from rice production can be used to produce high value-added silica materials with various applications. But present technologies suffer the shortages of using inorganic acid as the precipitating agent, complex salt-containing wastewater post-treatment, higher production cost, lower product quality, and without the recycling of process additives. In this paper, improved clean chemical precipitation characterizing of recycling the by-product and surfactant used is developed with the highest silica product yield of 99.3%, pore size (21-35 nm), and specific surface area (196-462 m²/g). After the by-product solution is reused 5 times, the yield of silica can still reach 99.1%. The recovery yield of surfactant is 95.3%. The properties of the prepared silica meet the standard of silica for specific applications. The process characterized the recycling of the by-product and surfactant in the process, greener CO₂ precipitant, ensuring the greenness, process efficiency, and low production cost. This opens up a new industrialization practical way for up-grading utilization of waste biomass and CO₂ containing industrial effluents.

Highlights

- High quality silica from rice husk ash is prepared by the recycling of the process assistant and by-product without any waste discharge.
- The commercial N, N-dimethyldodecylamine with switching surface activity is selected to achieve its recycling usage during the preparation, alleviating the consumption of surfactant.
- The environmentally friendly CO₂ from various industrial effluent gases is used as the precipitant and is converted into by-product NaHCO₃, then be converted into Na₂CO₃ for rice husk ash dissolution to attain the recycling use of NaHCO₃ and CO₂.
- This study gives new way for the utilization of agricultural waste and industrial waste gas to prepare high quality silica nano-material in a clean and economical way.

1. Introduction

Rice husk is a by-product of the rice milling process and is a kind of agricultural waste in all rice-producing countries. Rice husk is a biomaterial with the highest SiO₂ content. The content of SiO₂ is about 10.6% (Ding et al. 2005). As a kind of agricultural waste, rice husk not only occupies land, but also pollutes the environment, and has potential fire hazards. At present, the output of rice husk in the world is huge. Approximately 400 million tons produced every year. Rice husk can be burned to obtain rice husk ash, in which silica dispersed in rice husk ash and exists in hydrated amorphous form (Chandrasekhar et al. 2006; Shen 2017). If the rice husk ash is processed to produce high value-added silica or silicon-based materials, it can not only reduce environmental pollution but also create high economic benefits. Rice husk-based silica has unique and important application characteristics in various industrial fields,

because it has the advantages of large specific surface area, stable chemical properties, good electrical insulation, good heat resistance, good corrosion resistance, low thermal conductivity, high purity, and small particle size. It can be used as an amendment to remove heavy metals in soil and wastewater, and can also be used to clean organic pollutants in the gas through adsorption (Ahmad et al. 2014; Cai et al. 2013; Seyfferth et al. 2016), catalysis (Ersöz et al. 2014; Gan et al. 2013) and integrated processes (Adam et al. 2013; Zhang et al. 2017). It can also be used as tire fillers. Due to its good biocompatibility (Chen et al. 2018), it can also be used as food additives, cosmetics, and biomedical materials etc. (Belostozky et al. 2019; Chen et al. 2015; Gallardo 2015; Jin et al. 2020; Ssa et al. 2020; Zeng et al. 2014). At present, the typical preparation method of rice husk-based silica mainly adopts acidic precipitation technology with the assistance of surfactants for microstructure adjustment.

Chun et al. synthesized ordered mesoporous silica with various pore structures from rice husk by combining acid leaching, chemical dissolution, and co-assembly with additional surfactants (Jc et al. 2019).

Rohani Abu Bakar et al. produced high-purity silica from rice husk treated with hydrochloric acid and sulfuric acid by controlling the combustion temperature of rice husk (600–900°C) (Bakar et al. 2016).

Suresh Kumar Rajanna et al. prepared hollow particulate silica aerogel microspheres from rice husk ash by using an improved sol-gel/mineral-oil emulsion (containing dual surfactants) (Rajanna et al. 2015).

Li Dawei et al. used H_3PO_4 as a precipitant to prepare porous silica with high specific surface area from rice husk ash (Li et al. 2011).

An Dongmin et al. used rice husk ash as the silicon source, Na_2CO_3 as the silica extractant, and CO_2 waste gas as the precipitant to prepare silica powder (An et al. 2010).

Liang Guanqiao used 2-acrylamide-2-methylpropanesulfonic acid as the precipitant and dispersant to produce high-quality biomass silica from rice husk ash (Liang et al. 2018).

Although the above technologies prepared high-value-added silica from rice husk or rice husk ash, most of them used inorganic acids as the precipitant. Their use brought not only equipment corrosion, but also post-treatment of acid-containing wastewater. The surfactants used in the preparation process will be burned off during the roasting process, increasing production costs and causing pollution to the environment. Therefore, seeking a more efficient and cleaner method to synthesize high-quality silica from rice husk ash has important commercial value.

This paper proposes an efficient process for preparing high-quality SiO_2 from RHA with following features: (1) Water glass was prepared from RHA with NaOH - Na_2CO_3 mixture solution to achieve complete extraction of SiO_2 . (2) With CO_2 as the precipitant, the commercially available compound N, N-dimethyldodecylamine (DDA) with on-off surface-active was used as the structure regulator to prepare silica from water glass. By bubbling CO_2 , the non-surface-active DDA was converted into surface-active

ammonium bicarbonate (DDA- CO_2). Under ultrasound, surface-active ammonium bicarbonate was converted to non-surface-active DDA and CO_2 to ensure the recovery of DDA. The employment of DDA not only controlled the quality of the product but also ensured to increase the efficiency in this process by the recovery of DDA. (3) The by-product NaHCO_3 solution was converted into raw material (Na_2CO_3) by reacting with sodium hydroxide solution for reused as the material for rice husk ash dissolution, so that no extra waste solution was discharged in the process to ensure the cleanness and high efficiency.

2. Materials And Methods

2.1 Materials

Rice husk ash (high temperature and anaerobic carbonization of rice husk, 80–100 mesh, main components are SiO_2 and C, Shulan Jufeng biomass energy Co., LTD. China); Anhydrous sodium carbonate (industrial grade, 99.2%, Shandong Haihua Co., Ltd. China); Sodium hydroxide (industrial grade, 99.0%, Henan Qingyang environmental protection technology Co., Ltd. China); N, N-dimethyldodecylamine (industrial grade, 99.0%, Shanghai Jinjinle industrial Co., Ltd. China); CO_2 containing industrial effluent (main compositions are 40.0% CO_2 , about 5.0% O_2 , and 55.0% N_2 , Huaneng Jilin power generation Co., Ltd. China); Ethyl acetate (analytical grade, 99.5%, Tianjin Changmao chemical reagent chief, China); Hydrochloric acid (analytical grade, 36.5%, Tianjin Guangfu science and technology development Co., LTD. China); Methyl orange indicator (analytical grade, 99.0%, Tianjin Changmao chemical reagent chief, China) and Phenolphthalein indicator (analytical grade, 99.0%, Henan Jiuhe co-creation instrument Co., Ltd., China).

2.2 Experimental procedures

2.2.1 Preparation of water glass

50.0 g rice husk ash and 250 mL 24.0 wt% sodium carbonate solution with sodium hydroxide with a mass ratio of sodium hydroxide to sodium carbonate of 0.2: 1 into a was poured in 500 mL three-necked flask with a reflux condenser. The suspension was boiled at 100°C for 3 h, and vigorously stirred during the entire reaction. The suspension was filtered while it is hot, kept the temperature above 80°C . The solid residue was rinsed with distilled water. The filter cake was activated to get Carbon. The filtrate is the sodium silicate solution, i.e water glass, and was used for precipitation.

2.2.2 Preparation of silica powder

0.45 g DDA and all the water glass solution obtained above was poured in the precipitation reactor equipped with a thermostat, gas inlet, gas outlet and gas recovery device. Then it was flowed precipitant CO_2 at 5 L/h and at 60°C . After 2–3 h, the pH of the system reached 7–8, the reaction was stopped, and cooled the reactor to 45°C . The resulting solid-liquid mixture was first used to recover DDA. Then the remainder was filtered, the white precipitate was ultrasonically washed with distilled water for 2 times,

and it was calcinated at 500–600°C, at a heating rate of 5°C/min for 3 h to obtain rice husk ash-based silica powder. The filtrate was used for the recycling of the by-product.

2.2.3 Recovery and reuse of N, N-dimethyldodecylamine

The solid-liquid mixture at the precipitation step was sonicated at 45°C for 1 h, DDA-CO₂ was converted into DDA and CO₂, then let stand for 10 min, floating on the uppermost layer of the liquid surface, and it was recovered by separation and used for next run operation.

2.2.4 Recycling of the by-product solution

Determine the content of sodium carbonate and sodium bicarbonate in the by-product solution according to the method for determining the content of sodium carbonate and sodium bicarbonate in the mixed alkali. Through titration analysis, it is determined that the by-product solution mainly contains sodium bicarbonate and a small amount of sodium carbonate. The sodium hydroxide solution was first added to convert the sodium bicarbonate in the by-product solution into sodium carbonate, and then sodium hydroxide was added to adjust the ratio of sodium hydroxide to sodium carbonate to dissolve RHA.

All the filtrate obtained in the precipitation step was thoroughly mixed with 250 ml of 24% NaOH solution, then 24.0 g NaOH was added to the mixed solution and fully dissolved for the dissolution of RHA.

2.2.5 Process design

The whole process flow chart was shown in Fig. 1.

2.3 Characterizations

The powder X-ray diffraction (XRD) pattern of the sample was recorded on a bruker D8-advanced X-ray powder diffractometer using CuK α radiation ($\lambda = 0.1542$ nm) with scattering angles (2θ) of 10°-60°, operating at 40 keV, and a cathode current of 30 mA.

The Fourier transform infrared (FT-IR) spectra of the product were recorded on FT04-035 infrared spectrometer.

The specific surface area, pore diameter, pore volume measurements of silica were conducted on a Tristar II 3020 automatic specific surface and pore analyzer; silica specific surface area and pore size distribution were determined by the adsorption and desorption isotherms of nitrogen method. Sample was pretreated at 200°C vacuum 10 kPa 5 h. The low temperature nitrogen adsorption-stripping isothermal curves was used to calculate the specific surface area of the sample, according to the BJH model (take off) absorption with total pore volume and pore size distribution.

The internal microstructure of silica was characterized with JMS-5500 scanning electron microscope, before the micrographs were taken the samples were sputted with golden layer. An energy dispersive spectrometer (EDS) attached to the SEM instrument was used for elemental analysis.

SiO₂ yield is calculated as following:

$$SiO_2 yield = m_0 / m_1 * 100\%$$

Here m_0 is the mass of the SiO₂ obtained from the experiment, m_1 is the mass of SiO₂ in the rice husk ash analyzed. By analyzing the mass percentage of silica in rice husk ash is 46.6%.

3. Results And Discussion

3.1 Optimization of the process parameters of rice husk ash alkali dissolution

3.1.1 The effect of Na₂CO₃ solution concentration on silica yield

Liquid-solid ratio, alkali dissolution temperature, and alkali dissolution time were fixed at 5: 1, 100°C, and 3 h. The effect of the concentration of Na₂CO₃ on the yield of silica is shown in Fig. 2. With the increase of the concentration of the Na₂CO₃, the yield of silica gradually increased first and then decreased. When the concentration of the Na₂CO₃ reached 24.0 wt%, the yield of silica reached to the highest, up to 73.2%. When the concentration of Na₂CO₃ is further increased, the yield of silica decreased slightly.

This can be interpreted as the concentration of HCO₃⁻ and OH⁻ increased with the increase of Na₂CO₃ concentration. The increase of OH⁻ caused more silica to be precipitated from RHA. Therefore, after carbon dioxide acidic precipitation reaction, the yield of silica gradually increased. However, the solubility of HCO₃⁻ is lower than that of CO₃²⁻. When the concentration of the Na₂CO₃ solution exceeds 24.0 wt%, and a small amount of silica was precipitated and contained in the filter cake. Therefore, the yield of silica dropped slightly. The results showed that the optimal Na₂CO₃ solution concentration is 24.0 wt%.

3.1.2 The effect of the ratio of NaOH: Na₂CO₃ on the yield of silica

The concentration of sodium carbonate solution, liquid-solid ratio, alkali dissolution temperature, and alkali dissolution time were fixed at 24.0 wt%, 5: 1, 100°C, and 3 h. The effect of NaOH: Na₂CO₃ in the solution on the yield of silica is shown in Fig. 3. With the increase of the ratio of NaOH: Na₂CO₃, the yield of silica increased first and then stayed almost the same. When the ratio reached 0.2: 1, the yield of silica reached 99.3%. It can be explained as follows: with the increase of the ratio, the concentration of OH⁻ in the solution also increased, and the increase of OH⁻ caused all the silica in RHA to be converted into SiO₃²⁻ so that the yield of silica increased significantly. The ratio is further increased, the yield of silica nearly kept constant, as the dissolution of silica in rice husk ash is almost complete.

Compared with the result in 3.1.1, adding a small amount of sodium hydroxide to the sodium carbonate solution can significantly improve the yield of silica from 73.2–99.4%. Considering the cost factor, the ratio of NaOH: Na₂CO₃ is selected as 0.2: 1 in this study.

3.1.3 The effect of liquid-solid ratio on the yield of silica

The concentration of sodium carbonate solution, NaOH: Na₂CO₃, alkali dissolution temperature, and alkali dissolution time were fixed at 24.0 wt%, 0.2: 1, 100°C, and 3 h. The effect of the liquid-solid ratio on the yield of silica is shown in Fig. 4. With the increase of the liquid-solid ratio, the yield of silica first increased and then stayed almost the same. When the liquid-solid ratio reached 5: 1, the yield of silica reached 99.3%. It can be explained as: with the increase of liquid-solid ratio, RHA and the mixed solution were fully contacted, therefore the yield of silica increased. The liquid-solid ratio is further increased, the yield of silica was almost unchanged. Considering the preparation efficiency and cost, the liquid-solid ratio is selected as 5: 1 in this study.

3.1.4 The effect of alkali dissolution temperature on the yield of silica

The concentration of sodium carbonate solution, NaOH: Na₂CO₃, liquid-solid ratio, and alkali dissolution time were fixed at 24.0 wt%, 0.2: 1, 5: 1, and 3 h. The effect of dissolution temperature on the silica yield is shown in Fig. 5. With the increase of the temperature, the yield of silica increased first and then stayed almost the same. The yield of silica reached 99.3% at 100°C. However, when the temperature exceeds 100°C, it remained almost constant. The yield of silica reached the highest of 99.4%. Considering the cost of preparation, it is determined that 100°C is the optimal alkali dissolution temperature.

3.1.5 The effect of alkali dissolution time on the yield of silica

The concentration of sodium carbonate solution, NaOH: Na₂CO₃, liquid-solid ratio, and alkali dissolution temperature were fixed at 24.0 wt%, 0.2: 1, 5: 1, and 100°C. The effect of alkali dissolution time in the solution on the yield of silica is shown in Fig. 6. With the increase of the reaction time, the yield of silica increased first and then stayed almost the same. When the reaction time reached 3 h, the yield of silica reached 99.3%. When the time is longer than 3 h, the yield of silica did not increase significantly. The yield of silica reached the highest of 99.4%. Considering the cost of preparation, the alkali dissolution time is determined as 3 h.

Through the above research, the optimal process parameters of alkali dissolution were obtained as below: the concentration of Na₂CO₃ solution is 24.0 wt%, NaOH: Na₂CO₃ is 0.2: 1, the liquid-solid ratio is 5: 1, the alkali solution time is 3 h, the alkali solution temperature is 100°C, the silica yield is 99.3%.

3.2 Optimization of CO₂ precipitation parameters

3.2.1 The effect of N, N-dimethyldodecylamine dosage on the yield and specific surface area of silica

CO₂ acidification temperature, CO₂ flow rate, and calcination parameters were respectively fixed at 60°C, 5 L/h, calcination time 3 h, calcination temperature 550°C and heating rate 5°C/min. The effect of DDA dosage on the yield of silica is shown in Fig. 7a. With the increase of the DDA dosage, the yield of silica did not change much, and the yields were all around 99.3%. Because DDA does not react with sodium carbonate, sodium hydroxide and sodium silicate, it has no effect on the reaction mechanism of the formation of silica. It only plays a role in dispersing. Therefore, the yield of silica is almost unchanged.

The effect of DDA dosage on the specific surface area of silica was shown in Fig. 7b. With the increase of the DDA dosage, the specific surface area of silica increased first and then stayed almost the same. It reached the maximum of 462 m²/g at 0.45 g. With the increase of amount of DDA, the concentration of DDA-CO₂ in the mixed solution increased, preventing the agglomeration of silica particles and making them more uniformly dispersed, so the specific surface area gradually increased. However, when the dosage exceeds 0.45 g, the specific surface area of silica was almost unchanged. Because when the dosage of DDA is 0.45 g, the silica in the mixed solution has been completely dispersed, the specific surface area was almost unchanged. The DDA dosage has no effect on the yield of silica, but the specific surface area of silica reaches the maximum when the dosage of DDA is 0.45 g. Therefore, considering the cost factor, 0.45 g is chosen as the optimal dosage.

3.2.2 The effect of acidification temperature on the yield and specific surface area of silica

DDA dosage, CO₂ flow rate, and calcination parameters were respectively fixed at 0.45 g, 5 L/h, calcination time 3 h, calcination temperature 550°C and heating rate 5°C/min. The effect of CO₂ acidification temperature on the yield of silica is shown in Fig. 8a. With the increase of the acidification temperature, the yield of silica increased first and then stayed almost the same. The yield of silica reached the highest of 99.3% at 50°C. However, in the case where the acidification temperature exceeds 50°C, the yield of silica did not increase significantly. Because as the temperature increases, the reaction rate increases and the carbon dioxide reacts with the sodium silicate solution more completely, so the yield of silica gradually increases.

The effect of CO₂ acidification temperature on the specific surface area of silica is shown in Fig. 8b. It is seen that when the acidification temperature is adjusted from 30°C to 80°C, and the specific surface area of silica increased first and then decreased. It reached the maximum of 462 m²/g at 60°C. Because as the temperature increases, the solubility of DDA-CO₂ gradually increases, making the silica dispersion more uniform, and the specific surface area increases accordingly. However, when the temperature exceeds 60°C, the specific surface area of silica will decrease, because when the temperature is higher than 60°C,

partial DDA-CO₂ will be converted into DDA and CO₂, and the surface activity will lose, so the specific surface area will decrease.

The yield of silica at 50°C and 60°C is almost the same, but the specific surface area of silica at 60°C is higher than that at 50°C. Comprehensive consideration of the yield and specific surface area of silica, therefore, 60°C is determined as the optimal CO₂ acidification temperature.

3.2.3 The effect of CO₂ flow rate on the yield and specific surface area of silica

DDA dosage, CO₂ acidification temperature, and calcination parameters are respectively fixed at 0.45 g, 60°C, calcination time 3 h, calcination temperature 550°C and heating rate 5°C/min. The effect of the CO₂ flow rate on the yield of silica is shown in Fig. 9a. With the increase of the CO₂ flow rate, the yield of silica did not change much, and the yields were all-around 99.3%.

The effect of the CO₂ flow rate on the specific surface area of silica is shown in Fig. 9b. With the increase of the CO₂ flow rate, the specific surface area of silica was unchanged first and then decreased. It reached 462 m²/g at 5 L/h. The main reason is that the flow of CO₂ is small and the generation rate of SiO₂ is slow. The silica particles are more uniformly dispersed, so the specific surface area is larger. However, when the flow rate exceeds 5 L/h, because of the larger CO₂ flow rate accelerates the generation rate of SiO₂, agglomeration of silica particles occurs, and the specific surface area of silica decreased. The CO₂ flow rate has little effect on the yield of silica, but when the CO₂ flow rate is 3–5 L/h, the specific surface area of silica is larger. As the CO₂ flow rate is larger, the precipitation reaction time is shorter. Considering production efficiency, it is determined that 5 L/h is the optimal CO₂ flow rate.

Through the above research, the optimal process parameters of CO₂ acidification precipitation were determined as: DDA dosage is 0.45 g, the CO₂ acidification temperature is 60°C, and the CO₂ flow rate is 5 L/h. The product yield and specific surface area are respectively 99.3% and 462 m²/g.

3.3 Optimization of the calcination parameters

3.3.1 The effect of calcination time on the specific surface area of silica

Calcination temperature and heating rate were fixed at 550°C and 5°C/min. The effect of calcination time on the specific surface area of silica is shown in Fig. 10. The calcination time was within 2–4 h, the specific surface area of silica did not change much with the increase of calcination time, and the specific surface area was all-around 460 m²/g, it is determined that 3 h is the optimal calcination time.

3.3.2 The influence of calcination temperature on the specific surface area of silica.

Calcination time and heating rate were fixed at 3 h and 5°C/min. The effect of calcination temperature on the specific surface area of silica is shown in Fig. 11. With the increase of the calcination temperature, the specific surface area of silica increased first and then decreased. It reached the maximum of 462 m²/g at 550°C. As the temperature rises, the water in the silica volatilizes the pore structure increases and the specific surface area of the silica increases. However, when the temperature is higher than 550°C, the specific surface area of silica decreased. Because when the temperature is higher than 550°C, the pore structure of silica is destroyed and the specific surface area became smaller. Therefore, 550°C is determined as the optimal calcination temperature.

3.3.3 The effect of heating rate on the specific surface area of silica

Calcination time and calcination temperature were fixed at 3 h and 550°C. The effect of heating rate on the specific surface area of silica is shown in Fig. 12. With the increase of the heating rate, the specific surface area of silica was unchanged first and then decreased. It reached 462 m²/g at 5°C/min. Because when the heating rate is higher than 5°C/min, the pore structure of silica is destroyed and the specific surface area became smaller. To shorten the heating time, therefore, it is determined that 5°C/min is the optimal heating rate.

Through the above research, the optimal calcination parameters were determined as calcination time is 3 h, the calcination temperature is 550°C, the heating rate is 5°C/min. The product yield and specific surface area are respectively 99.3% and 462 m²/g.

3.4 Optimization of N, N-dimethyldodecylamine recovery process parameters

DDA possessed the surface activity switching property in the participation of CO₂, providing the possibility of recovery in the preparation. DDA was converted into ammonium bicarbonate (DDA-CO₂) by bubbling carbon dioxide and converted into DDA and CO₂ under ultrasound at 45°C. Then let stand for 10 min, DDA was separated and recovered by a separatory funnel. The recovered DDA and the CO₂ produced by the process were used in the next run of the CO₂ acidification reaction. It was founded that the recovery yield of DDA is prominently related to temperature and ultrasonic time. The recovery rate of DDA is calculated as follows: the separated DDA was extracted with ethyl acetate and distilled under reduced pressure at 90°C for 1 h. The calculation formula is:

$$\text{DDA recovery yield} = m/m_1 * 100$$

Where m is the mass of DDA recovered in the experiment, and m_1 is the mass of DDA added in the experiment.

The DDA surface activity switching process in the SiO₂ preparation is shown in Fig. 13.

The FT-IR diagrams of the recovered product and DDA are shown in Fig. 14, Fig. 14 showed that the recovered product DDA and the recovered are the same structure.

3.4.1 The effect of ultrasound time on the recovery of N, N-dimethyldodecylamine

Under the optimal preparation parameters, the ultrasonic temperature was fixed at 45°C. The effect of ultrasonic time on the recovery yield of DDA is shown in Fig. 15a. With the increase of the ultrasonic time, the recovery yield of DDA increased first and then stayed almost the same. It reached the maximum of 95.3% at 60 min. Because the conversion of DDA-CO₂ into DDA and CO₂ becomes more complete with the increase of ultrasound time, the recovery yield of DDA increased. When the ultrasonic time is higher than 60 min, the recovery yield remained constant. Therefore, 60 min is determined as the optimal ultrasound time.

3.4.2 The effect of ultrasonic temperature on the recovery yield of N, N-dimethyldodecylamine

Under the optimal preparation parameters, the ultrasonic time was fixed at 60 min. The effect of different ultrasonic temperature on the recovery of DDA is shown in Fig. 15b. It is seen that when the ultrasonic temperature is changed from 25°C to 50°C, and the recovery yield of DDA increased first and then stayed almost the same. It reached the maximum of 95.3% at 45°C. Because as the temperature increases, the recovery rate of DDA-CO₂ to DDA and CO₂ is faster and more complete, the recovery yield of DDA increased. When the temperature exceeds 45°C, a significant increase in the yield of silica was not observed. Therefore, it is determined that 45°C is the optimal ultrasonic temperature.

Through the above research, the optimal DDA recovery process parameters were determined as ultrasound time is 60 min, ultrasonic temperature is 45°C, the DDA recovery yield is 95.3%.

3.5 The recycling of the by-product solution on the yield and specific surface area of silica

The effect of by-product solution reused times on the yield of silica is shown in Fig. 16a. Within 1–5 times, as reused times increase, the yield of silica did not change much, and the yields were 99.3%. The effect of by-product solution reused times on the specific surface area of silica is shown in Fig. 16b. Within 1–5 times, with the increase of reused times, the specific surface area of silica was almost unchanged, all around 460 m²/g.

3.6 Experimental fundamental principles

The rice husk-based silica powder is prepared by the precipitation method. The basic principle is:

(1) mixed Alkaline dissolution of rice husk ash:

(2) Carbon dioxide acidic precipitation:

(3) Calcination:

(4) The recovery of N, N-dimethyldodecylamine:

DDA possessed with on-off surface activity. It was protonated into a surface-active form by reacting with CO_2 to form ammonium bicarbonate (DDA- CO_2), then this bicarbonate can be converted can convert into DDA (without surface activity) with the assistance of ultrasonic at 45°C, this inter-transformation can be monitored by measuring the conductivity of the aqueous solution. The reaction formula is as follows:

(5) The by-product solution recycling:

The by-product solution was converted into sodium carbonate solution by adding sodium hydroxide solution. The reaction formula is as follows:

3.7 Structural characteristics of silica powder product

The XRD pattern of the silica powder is shown in Fig. 17a. It can be seen from the figure that only an amorphous diffraction peak appears at a low diffraction angle of about 23°, without sharp crystal diffraction peaks. This is a typical amorphous structure and the absence of any ordered crystal structure indicates the relatively high disordered structure of silica. The silica powder was confirmed by the FT-IR spectrum in Fig. 17b. The absorption bands at 3442 cm^{-1} and 1630 cm^{-1} are caused by the H-O-H stretching and bending modes of the adsorbed water, respectively. The asymmetry, symmetry, and

bending modes of SiO₂ are the peaks at 1104 cm⁻¹, 803 cm⁻¹ and 471 cm⁻¹, respectively (Nagaraja et al. 2006). According to the N₂ isothermal adsorption-desorption curve (BET) in Fig. 18a, the specific surface area of the products is 196 m²/g, 270 m²/g, 392 m²/g, 462 m²/g, respectively. The pore-pore diameter curve of SiO₂ is shown in Fig. 18b. The average pore sizes are 34.1 nm, 21.6 nm, 28.2 nm, 21.6 nm, respectively. The data shows that the specific surface area and pore diameter of the silica synthesized by the modified method are controllable and suitable for applications in specific occasions. Figure 19 is the SEM image of the product silica. It can be clearly seen from the figure that the shape of the silica particles prepared by this method is approximately spherical, with an average particle size of 200 nm. In the presence of DDA, porous silica particles are obtained. Therefore, this is the reason why this method can significantly increase the value of the specific surface area of precipitated silica. Because DDA can easily form surface-active DDA-CO₂ in water when CO₂ is introduced, it can effectively prevent the agglomeration of silica particles and form silica particles with pore structure.

Figure 20 is the SEM-EDS image of the product silicon dioxide. It can be seen from the image that high-purity silicon dioxide is successfully obtained through this process.

Table 1
Property comparison of the product and commercial silica for different areas

	SiO ₂ content (%)	Oil absorption value (g/100 g)	Specific surface area (m/g)	Drying loss ≤ (%)	Ignition loss ≤ (%)	Heavy metal content ≤ (%)
Product	99.1	250–320	196–462	2.5	2.0	0.0001
Tires	92.0	200–300	150–200	7.0	7.0	—
Food additives	99.0	250–300	300–350	2.5	2.0	0.0003
Cosmetics	99.0	350–400	350–400	5.0	2.5	0.0003
Biomedical materials	98.0	400–450	400–450	5.0	2.5	0.0003

Table 1 listed a comparison results of the properties of the product and with various commercial used silica. The performance indicators of silica are determined according to the national standard method (ISO 5794-1). It is seen that the product (silica) prepared in this study fully meets the standards of commercial silica for food additives (GB 25576 – 2020) and tire fillers (ISO 574-1), and mostly meets the standards of commercial silica for cosmetics and biomedical materials.

4. Conclusion

Rice husk ash was successfully transformed to high-quality silica by alkali dissolution, CO₂ precipitation and calcination. The preparation features the employment of environment-friendly precipitator CO₂ from various industrial sources; and the recycling of the by-product NaHCO₃ and DDA, ensuring the low cost

and greenness and high efficiency of the preparation and favoring the alleviation of CO₂ emissions and utilization. The silica quality obtained with the optimal process parameters is qualified for use in various high-end fields, which opens up a new way for the high-quality utilization of rice husk, and is suitable for industrial production, and has practical reference solution for the environmental protection concern and industrial application of agricultural wastes.

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Figures

Figure 1

Flow chart for preparing silica powder from RHA

Figure 2

Effect of the concentration of Na₂CO₃ solution on silica yield

Figure 3

Effect of the ratio of NaOH: Na₂CO₃ on the yield of silica

Figure 4

Effect of liquid-solid ratio on the yield of silica

Figure 5

Effect of alkali dissolution temperature on the yield of silica

Figure 6

Effect of alkali dissolution time on the yield of silica

Figure 7

Effect of DDA dosage on the yield and specific surface area of silica, yield (a), and specific surface area (b)

Figure 8

Effect of acidification temperature on the yield and specific surface area of silica, yield (a), and specific surface area (b)

Figure 9

Effect of CO₂ flow rate on the yield and specific surface area of silica, yield (a), and specific surface area (b)

Figure 10

Effect of calcination time on the specific surface area of silica

Figure 11

Effect of calcination temperature on the specific surface area of silica

Figure 12

Effect of calcination heating rate on the specific surface area of silica

Figure 13

DDA surface-active switching process

Figure 14

Recovered product (a), and DDA (b)

Figure 15

Effect of ultrasound time and temperature on the recovery yield of DDA, ultrasound time (a), and ultrasound temperature (b)

Figure 16

Effect of by-product solution reused times on the yield and specific surface area of silica, yield (a), and specific surface area (b)

Figure 17

XRD pattern of silica (a), and FT-IR spectra of silica (b)

Figure 18

Adsorption and desorption isotherms of SiO₂ (a), and pore volume-pore diameter curve of SiO₂ (b)

Figure 19

SEM image of the silica

Figure 20

SEM-EDS pattern of the silica

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