



A green route to preparation of silica powders with rice husk ash and waste gas

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ABSTRACT

The objective of the present work is to develop a green procedure for preparation of silica powders from rice husk ash (RHA) via a carbonation route. The raw materials, RHA and waste gas, were obtained from the power plant. Na₂CO₃ was used as the silica extraction reagent and waste gas was the precipitator. The silicon dioxide extraction yield reached 72.52% and was affected by impregnation ratio, concentration of Na₂CO₃ solution and reaction time. The microstructures of the as-obtained silica powders were characterized by X-ray diffraction (XRD) and infrared spectra (IR). The mineral contents of RHA and product were investigated by inductively coupled plasma (ICP) emission spectroscopy. In the whole silica extraction process, extraction reagent can be reused through appended a small quantity of Na₂CO₃ to its initial concentration. The synthetic procedure is straightforward, inexpensive and environment-friendly, which was suitable for large-scale production.

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1. Introduction

Silica (SiO₂) is a basic raw material that is widely used in electronics, ceramic, and polymer material industries. Due to their small-diameter, silica powders have many technological applications, such as thixotropic agents, thermal insulators, composite fillers, etc. [1].

Rice husk is an agricultural by-product abundantly available in rice-producing countries that on average accounts for 20% of the paddy produced, on weight basis. An increasing application of rice husk is used as fuel in the power plant, due to its high calorific power (approximate 13–16 MJ/kg) [2–5]. In this combustion, rice husk ash (RHA) is produced. RHA is usually black or gray in color and has a light weight, therefore, the disposal of bulky RHA could be a problem. In some areas, a large amount of RHA is treated as waste and disposed at landfill site, which leads to air and water pollution. The airborne particles have been linked to respiratory disease in humans [6]. Therefore, if it is not disposed in time, it will become a serious environmental problem. Recent investigations on the production of the RHA with high activity and the possible application of it in cement and concrete have been made by many researches [7–10]. All the results reveal that burning rice husk under well-defined conditions is the only way to obtain this active RHA. The sensitivity of burning conditions is the primary reason that prevents the widespread use of this material as pozzolan [11,12]. Several researchers have utilized RHA to prepare zeolites

and mesoporous silica [13–16]. Some utilize RHA as an adsorbent to adsorb metal ions such as Cd²⁺, Zn²⁺, and Ni²⁺, and heavy metal such as lead and mercury from aqueous solution [17–19]. Some organic matters, such as Congo red, vacuum pump oil, palmytic acid, Indigo Carmine dye, Brilliant Green dye and so on, can also be adsorbed by RHA [20–23]. However, the final disposal of the RHA after adsorption has not been reported. Recent studies have demonstrated that the RHA can be an economically available raw material for production of silica gels and powders [24–28]. While the classical method for the preparation of silica powders generally employs acid with sodium silicate, which is currently manufactured by smelting quartz sand with sodium carbonate at 1300 °C [29,30], or manufactured by NaOH extraction from RHA [31]. With the aforementioned method, high temperature requires high energy and the utilization of acid especially the volatile hydrochloric acid not only corrupts the reaction equipment but also brings an extra financial cost and pollutes environment, moreover, silica xerogel is usually obtained through acid precipitation.

On the other hand, the waste gas, which usually contains about 20–40% carbon dioxide (CO₂), is released during rice husk burning in the power plant. As we all know that CO₂ is a major greenhouse gas with significant contribution to global warming [32]. Hence, it is necessary to find a proper strategy for its handling, and utilization. Removal of CO₂ from different industrial gas streams is becoming increasingly important in recent years. Several papers have reported the utilization of CO₂ gas for various applications like power generation, natural gas, stack gas and heating as well as closed-circuit breathing systems for use in confined spaces such as manned space shuttles [33–37]. The recovered CO₂, with different degrees of purity, has also numerous applications in the chem-

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ical industry. Micro- and nanoporous silica materials have been prepared using supercritical carbon dioxide as solvent [38–41]. Chattopadhyay and Gupta prepared silica particles by injecting a water-in-oil microemulsion of an aqueous sodium silicate solution into supercritical CO₂ [42]. Cai et al. has synthesized silica powders by pressured carbonation [43].

In order to reduce the operating cost and protect environment, an alternative and more efficient route to prepare silica powders would be of considerable commercial interest. In this paper, a green method was developed to extract silica from RHA with Na₂CO₃ and prepare silica powders through a carbonation route. Herein, Na₂CO₃ was used as silica extraction reagent and CO₂, which was obtained after the purifying of the waste gas, was the precipitating reagent. It is a feasible way to synthesize silica powders with industrial wastes RHA and exhaust gas compared with the conventional ones.

2. Materials and methods

2.1. Materials

All chemicals were analytical grade and used without further purification. Anhydrous sodium carbonate (Na₂CO₃) and hydrochloric acid (HCl) were purchased from the Beijing Reagent Factory of China. The rice husk ash (RHA) was from Liuan of Anhui Province in China. Distilled water was applied for all synthesis and treatment processes.

2.2. Analysis of the composition of RHA

The analysis of minerals composition was referred to Kalapathy et al. [44], and the content of silicon dioxide was measured according to the China National Standards GB10518-89. 5 g of RHA was added into 50 ml of 1.0 mol/l HCl solution, the suspension was then boiled for 2 h under stirring. The suspension was filtered and the solid residue was washed by distilled water to remove the metallic ions completely. The filtrate and washings were collected for the analysis of metallic content. The solid residue, which was used for further silica extraction, was dried in an oven at 120 °C for 12 h.

30.00 g of the pretreated RHA was put into a plastic reactor, 150 ml of 3.0 mol/l HF and 10 ml of H₂SO₄ was then added into the reactor to dissolve silicon dioxide. The suspension was filtered and the residue was washed by distilled water to be neutral. The residue was dried in an oven at 120 °C for 12 h for further analysis, the content of silicon dioxide can be calculated by the formula as follows: $(m_o - m)/m_o$, where m_o is the weight of RHA after acid pretreatment and m is the weight of residue after HF reaction.

2.3. Silica extraction

30.00 g of the RHA after acid pretreatment was put into a three-necked flask, and 150 ml of certain concentration of Na₂CO₃ solution was then added into the reactor. The suspension was boiled for 4 h under reflux condenser, and vigorous stirring was applied during the whole reaction process. The suspension was filtered, and solid residue was washed with hot water. The temperature of the filtrate and the whole filtration process was kept above 90 °C. Finally, the filtrate was moved to another reactor with an aspect ratio of 15.

2.4. Preparation of silica powders

The obtained filtrate was kept at 85 °, and the waste gas after purifying was then introduced into the reactor through a tube.

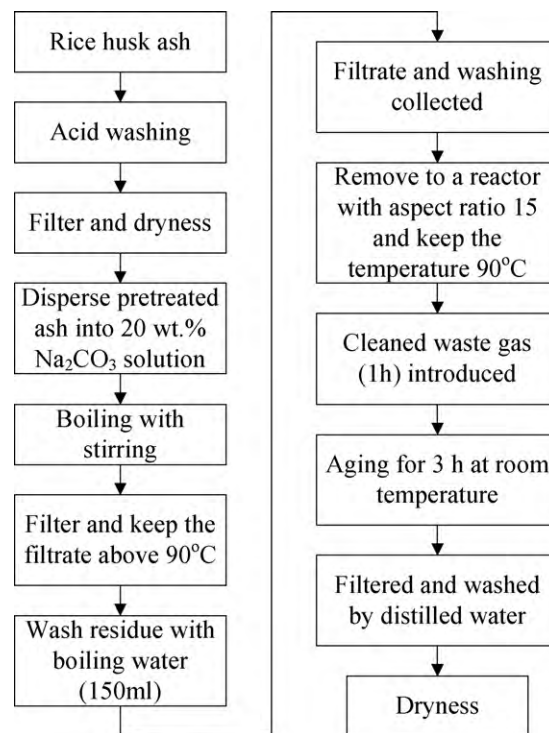


Fig. 1. Flow diagram of the procedure used to produce silica powders from RHA.

The resulting slurry was kept aging for 3 h at room temperature after carbonation for 60 min, and then was filtered using a pump. The precipitate was washed by distilled water and then was dried at 120 °C for 24 h. The whole experimental process was shown in Fig. 1.

2.5. Single factor test

The silica yield was mainly affected by the concentration of Na₂CO₃ solution, the impregnation ratio and the reaction time. To find the optimal experimental conditions, the extraction time was varied from 1 to 8 h while fixing other conditions, the concentration of Na₂CO₃ was varied from 10 to 30 wt.%, the impregnation ratio was from 5:1 to 10:1, and carbonation time was from 0 to 80 min.

2.6. Moisture analysis

Approximate 1.0 g of silica powders sample was heated in aluminum moisture pans at 130 ° for 1 h. The sample was cooled in a desiccator and weighed. The percent of weight loss was recorded as the moisture content of sample. The examination was performed in triplicate.

2.7. Characterization

Mineral composition of the RHA and silica powders was determined by atomic emission measurements using ICP emission spectroscopy (Perkin-Elmer Optima 3300 DV). The crystalline phase of the synthesized silica powders was characterized by the X-ray diffraction (XRD), using Cu K α ($\lambda = 1.54056 \text{ \AA}$) radiation on a SHIMADZU-6000 X-ray diffractometer. Fourier transform-infrared spectroscopy (FTIR) experiment was carried out on a Bruker FT 5DX (Nicolet) spectrometer employing the KBr pellet method.

Table 1
The composition of RHA.

Composition	Value
K ₂ O	1.46 wt.%
CaO	0.45 wt.%
Na ₂ O	0.09 wt.%
MgO	0.17 wt.%
Al ₂ O ₃	0.42 wt.%
ZnO	0.08 wt.%
Fe ₂ O ₃	0.19 wt.%
MnO ₂	0.10 wt.%
CuO	375 ppm
TiO ₂	13 ppm
SiO ₂	78.44 wt.%
C	18.24 wt.%
Others	0.36 wt.%

3. Results and discussion

3.1. The composition analysis of RHA

Composition of minerals leached from RHA by acid pretreatment was shown in Table 1. The gross weight of silicon dioxide in the RHA was 78.44 wt.%, and the residual was carbon and other impurities. The conclusion that preliminary leaching of rice husks with a solution of HCl, boiled before thermal treatment, made by Krishnarao et al. [45,12,46] has been proved to be an effective way in substantially removing most of the metallic impurities and producing ash silica completely white in color.

3.2. Effect of the concentration of Na₂CO₃ solution on silica yield

The yield of silica affected by different concentrations of Na₂CO₃ was shown in Fig. 2. When the other three factors (impregnation ratio, extraction and carbonation time) were fixed at 5:1, 4 h and 60 min, the yield of silica gradually increased with the increasing of Na₂CO₃ concentration, and reached the maximum value (72.52%) at the concentration of 20 wt.% Na₂CO₃, but further increment of Na₂CO₃ concentration did not give an increase in silica yield. It can be explained as follows: the reactions (a, b and c) occur in the Na₂CO₃ solution, and the concentrations of HCO₃⁻ and OH⁻ increase with the increasing of Na₂CO₃ concentration. The increment of OH⁻ lead to more silica leached out from RHA, therefore, the content of SiO₃²⁻ increased, which accelerated the

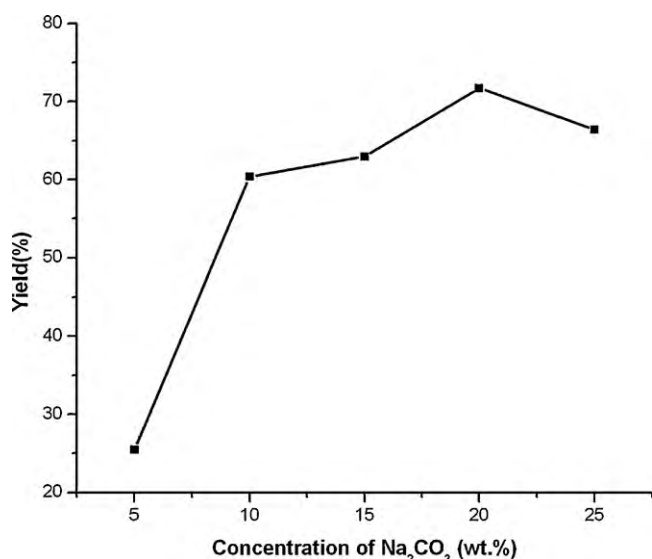


Fig. 2. The effect of the concentration of Na₂CO₃ solution on silica yield.

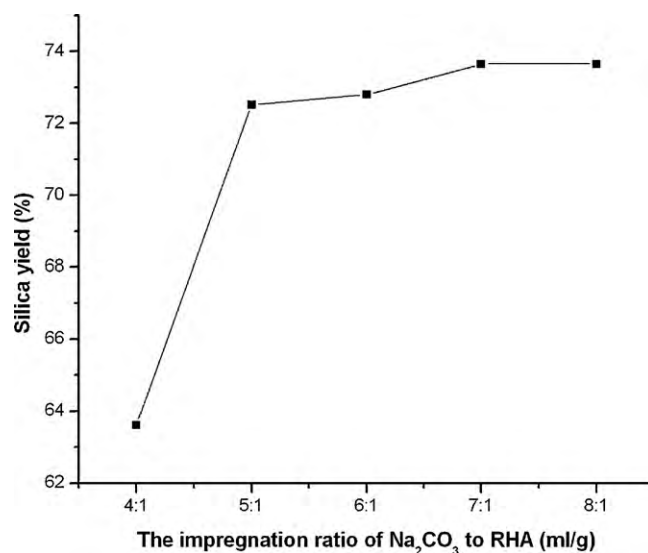
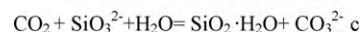
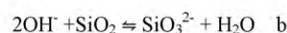
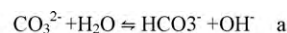


Fig. 3. The effect of the impregnation ratio on silica yield.

reaction processing, so the yield of silica was gradually increased. However, the solubility of HCO₃⁻ is weaker than CO₃²⁻, and the increasing of HCO₃⁻ lead to the separating out of silica in the residue before filtering the suspension, so the yield of silica slightly decreased when the concentration of Na₂CO₃ was above 20 wt.%. The results confirmed that the optimal Na₂CO₃ concentration was 20 wt.%.



3.3. Effect of the impregnation ratio on silica yield

The yield of silica affected by different impregnation ratios of Na₂CO₃ solution to RHA (ml/g) was shown in Fig. 3. When the other three factors (Na₂CO₃ concentration, extraction and carbonation time) were fixed at 20 wt.%, 4 h, and 60 min, the yield of silica increased with the increment of impregnation ratio. However, higher impregnation ratio (above 5:1) could not give an appreciable increase in silica yield, which reached a limited value of 73.2%. So the impregnation ratio of 5:1 was used in this study.

3.4. Effect of the reaction time on the silica yield

To find the effect of extraction time on the yield of silica powders, the extraction time was varied from 2 to 9 h, while fixing the other three factors (Na₂CO₃ concentration, impregnation ratio and carbonation time) at 20 wt.%, 5:1 and 60 min, respectively. The yield of silica increased with the increasing of extraction time as shown in Fig. 4. However, no significant increase of silica extraction yield was observed at longer extraction time than 4 h, so 4 h was confirmed to be the optimal extraction time.

The effect of carbonation time on the yield of silica was also investigated, which was shown in Fig. 5. Partial silica was separated out from the filtrate when the suspension was filtered, and the silica yield increased with the increasing carbonation time, when carbonation time was from 0 to 60 min. However, no significant increase of silica yield was observed above 60 min. So it was confirmed that the optimal carbonation time was 60 min.

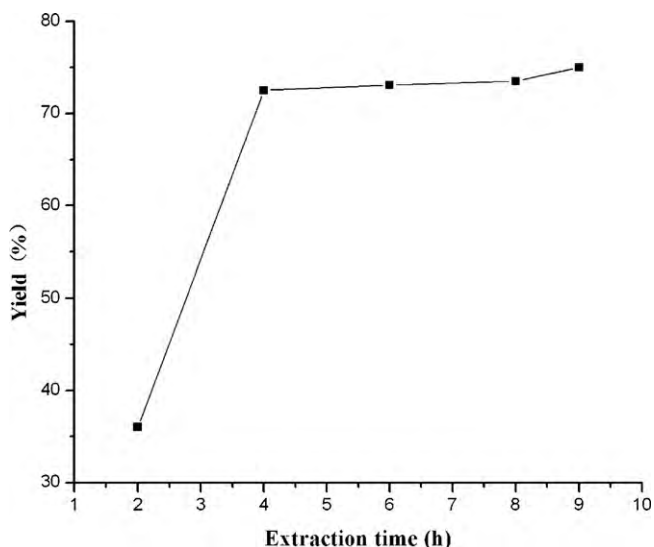


Fig. 4. The effect of the extraction time on silica yield.

3.5. The reuse of Na_2CO_3 and its effect on the yield of silica

The variation of Na_2CO_3 concentration with the recycle times was shown in Fig. 6a. The content of Na_2CO_3 in filtrate decreased with an increasing of recycle times, and then slowly down to 84.5% when the recycle times reached 5. The content of Na_2CO_3 in the filtrate was prone to be steady, and only about 16.5% Na_2CO_3 was needed to be appended to the initial concentration to realize its reuse. The yield of silica using the recycle filtrate was shown in Fig. 6b. The trend of curve was the same as the content of Na_2CO_3 in filtrate, first slowly down then was prone to be steady to about 60%. As could be explained that part Na_2SiO_3 was residual in filtrate after the initial use of Na_2CO_3 because the pH was 10 when the first carbonation reached the end point. The concentration of Na_2SiO_3 in filtrate increased slowly with the increasing of the recycle times initially, which lead to the increasing of viscosity of the recycle solution. As a result, the content of silica leached out from RHA was decreased, but the concentration of Na_2SiO_3 in filtrate was prone to be steady with the increasing of the recycle times, so the yield of silica was also prone to be steady.

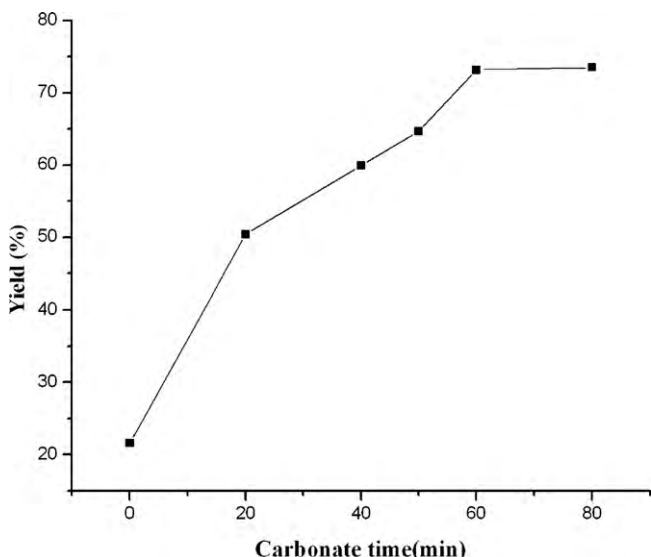


Fig. 5. The effect of the carbonation time on silica yield.

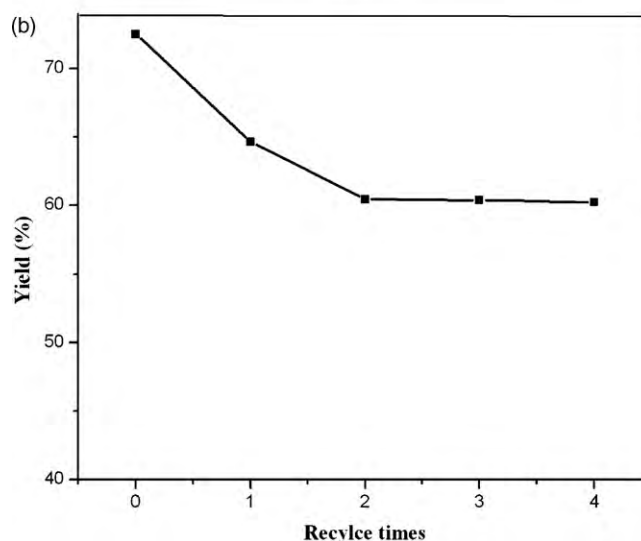
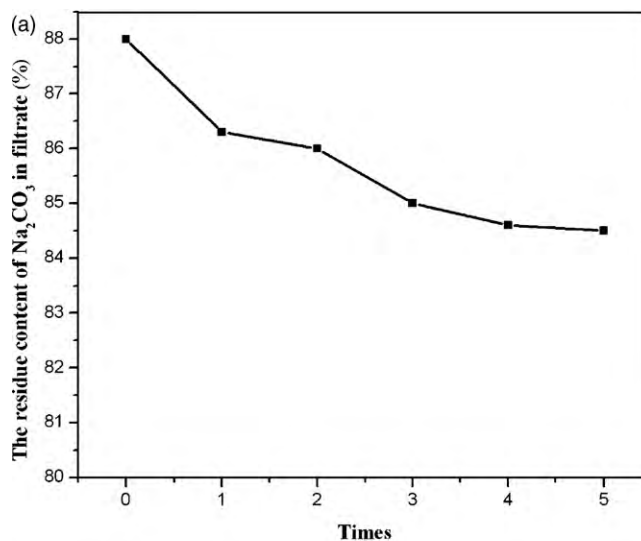


Fig. 6. The concentration variation of Na_2CO_3 solution with the recycle times (a). The effect of recycles time on the silica yield (b).

3.6. The composition and structural features of silica powders

Data in Table 2 showed that the metal composition of the as-obtained silica powders by ICP measurement. The silica and moisture content of the powders produced from RHA were 98.20% and 1.58%, respectively. It was confirmed that the metal oxides were removed efficiently after acid pretreatment. The X-ray diffraction pattern of silica powders was shown in Fig. 7a. It was a typical

Table 2
Mineral content of silica powders prepared from RHA.

Composition	Value (wt.%)
K_2O	0.0037
Na_2O	0.0109
CaO	0.0011
MgO	0.0012
Al_2O_3	0.0019
Fe_2O_3	0.0023
ZnO	0.0000
MnO_2	0.0009
CuO	0.0000
TiO_2	0.0000
Sum	0.022

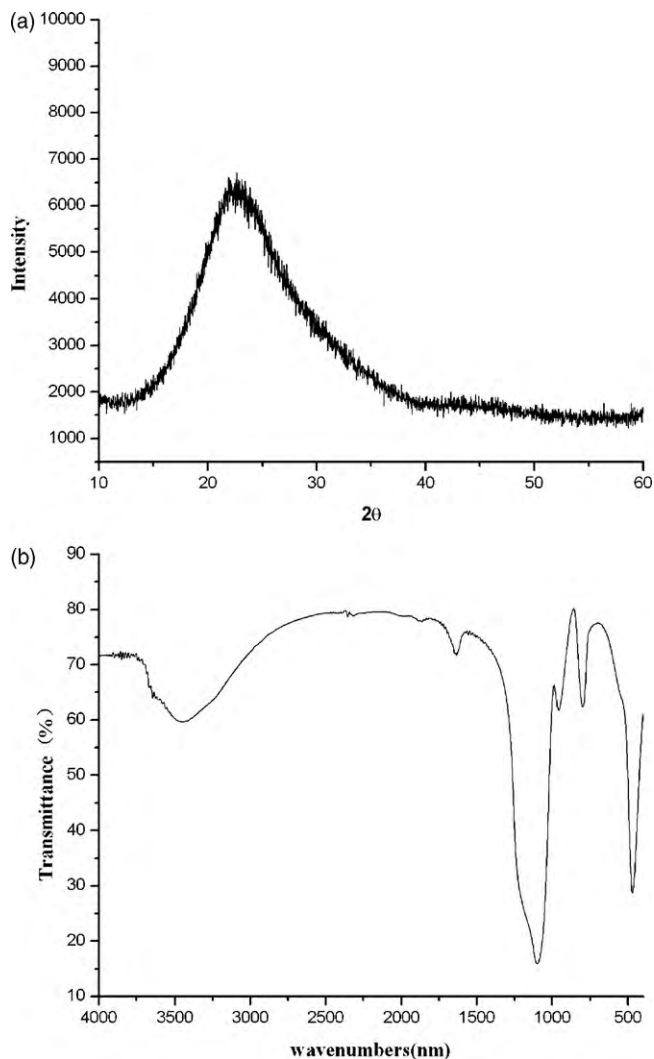


Fig. 7. X-ray diffraction pattern of silica produced from RHA (a). Fourier transform infrared spectra of silica produced from RHA (b).

amorphous structure, and the absence of any ordered crystalline structure indicated relative high disordered structure of silica. The silica powders were confirmed by FT-IR examination in Fig. 7b. The absorption bands at 3416 and 1639 cm^{-1} were due to the H–O–H stretching and bending modes of the adsorbed water, respectively. The peaks at 1093 , 788 , and 466 cm^{-1} were due to the asymmetric, symmetric and the bending modes of SiO_2 respectively [47].

4. Conclusions

Silica powders were successfully prepared with industrial wastes RHA and CO_2 through a green route. The silicon dioxide yield can reach 72.52% under the optimum extracting conditions which were 20 wt.% of Na_2CO_3 concentration, 5:1 of impregnation ratio, 4 h of extraction time and 60 min of carbonation time. The silicon dioxide and moisture content of the obtained powders were 98.20% and 1.58%, respectively. Moreover, it was a sustainable way to realize scale production as the extraction reagent Na_2CO_3 could reuse in the silica extraction process.

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