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Pilot-scale continuous biogenic silica extraction from rice husk by one-pot alkali hydrothermal treatment and ball milling

Ji Yeon Park^{1,2}, Yang Mo Gu^{1,2}, Jinyoung Chun¹, Byoung-In Sang² and Jin Hyung Lee^{1*}

Abstract

Background Rice husk is the most silicon-rich renewable biomass and can be used as a raw material for producing silicon-based materials. With the increasing interest in utilizing rice husk as a renewable resource, the development of a robust silica extraction method is required. In this study, a one-pot alkali hydrothermal and ball-milling continuous silica extraction method was developed at the pilot scale.

Results Three residence times (50, 100, and 150 min) were selected to compare the performance of the continuous extraction process depending on the residence time. The silica production was 4.09, 2.67, and 2.22 kg day⁻¹ while the silica extraction yield was 52.8, 69.1, and 86.0% at resident times of 50, 100, and 150 min, respectively. The energy consumption for producing 1 kg of silica from rice husk was 51.6, 47.7, and 47.4 MJ kg⁻¹ at resident times of 50, 100, and 150 min, respectively. The one-pot continuous silica extraction process was performed for 150 h to verify the stability of the process. During long-term operation, the process exhibited a constant solid content and stable silica extraction yield. The silicate solution obtained by the one-pot continuous process was successfully used to synthesize size-controlled spherical silica particles, which had a purity of 99.1 wt% and amorphous structure.

Conclusions Overall, this study presents a novel continuous silica extraction method for the efficient recovery of silica from rice husk-based biorefineries.

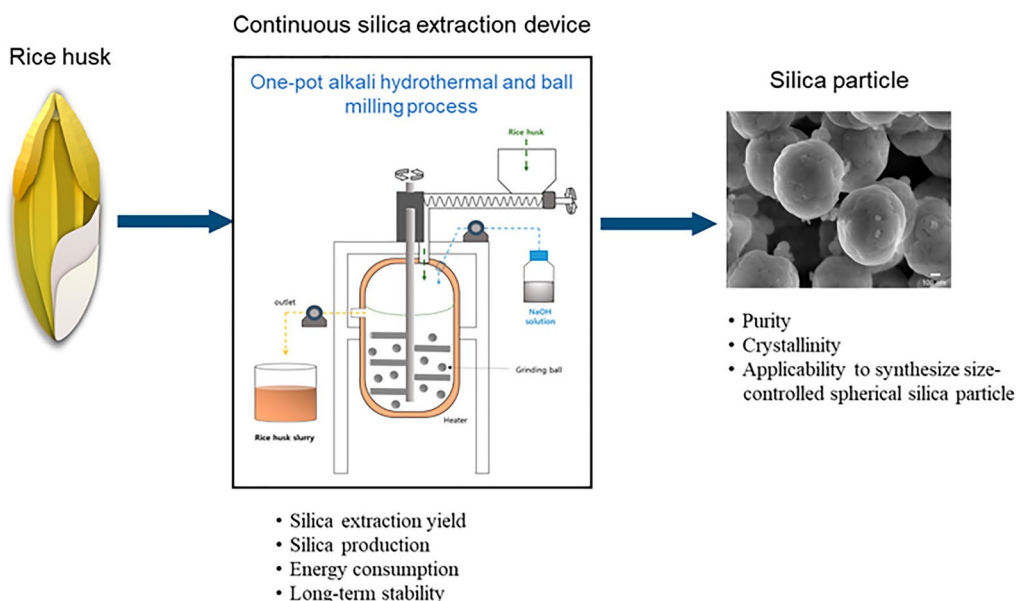
Keywords Rice husk, Biogenic silica, Continuous extraction, Pilot-scale, One-pot treatment, Ball milling, Alkaline hydrothermal

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Graphical abstract



Background

The utilization of renewable resources such as lignocellulosic biomass to synthesize high-value-added materials is an attractive subject that has become increasingly important [1]. Thus, rice husk has attracted considerable attention as a renewable source because of their high silica content [2]. Rice husk has an average silica content of 10–20% [3]. Rice husk-derived silica can be used as a low-cost precursor for high-value-added silica particles [4–6] or Si-based materials [7]. Rice husk is an attractive industrial resource because it is produced in large quantities as a byproduct of rice mill plants and is already dried, which can reduce transportation and drying costs.

To utilize rice husk silica, it should be extracted from the rice husk bulk material. Three methods, namely combustion, acid leaching, and alkali extraction, have been used to extract silica from rice husk [2]. Combustion is the easiest and most extensively used method for obtaining high-purity silica from rice husk. This method involves the thermal decomposition of the carbon in rice husk, forming rice husk ash, which mainly consists of silica. Acid leaching involves the dissolution of metallic impurities using a strong acid solution, yielding high-purity silica in the solid phase. Alkali extraction solubilizes silica in an alkali solution and separates it from the other components. Subsequently, the soluble silica can be precipitated using an acidic medium. In general, sodium hydroxide is used to extract silica from rice husk,

forming sodium silicate, which can be used as a precursor for Si-based materials [4–6]. Recently, we investigated the effect of rice husk silica extraction methods on the biocompatibility of rice husk silica in six different human and mouse cell lines [8]. The study demonstrated that the presence of residual carbon before calcination negatively affected the biocompatibility of rice husk silica. Moreover, among the three extraction methods, alkali extraction was the most suitable method for increasing the biocompatibility of rice husk silica. Previously, a two-stage continuous process was developed at the laboratory scale to effectively extract silica from rice husk [9]. This process involved alkali hydrothermal and ball milling processes. One of the disadvantages of handling lignocellulosic biomass is its low density; for example, rice husk has a density of 90–150 kg m⁻³ [10]. This property leads to high transportation costs and complicates the conveying processes. The combined ball milling and alkali hydrothermal method produce a rice husk slurry that can be easily conveyed using a fluid pump. This study demonstrated the feasibility of a continuous process; however, it was not a completely continuous process and the study was conducted at the lab scale.

In this study, we develop a one-pot continuous silica extraction reactor for ball milling and alkali leaching at the pilot scale. The continuous process has several advantages, such as narrow product specifications, reduced production costs, and increased productivity [9], which

are essential for industrial applications. In this context, this study demonstrates the feasibility of a continuous silica extraction process for industrial applications and advances the industrial utilization of rice-husk-derived silica. To the best of our knowledge, this is the first attempt to continuously extract silica from rice husk at the pilot scale.

Materials and methods

Materials

Rice husk was supplied by a rice processing facility in the Chungbuk province in the Republic of Korea and was harvested in 2021. Sodium hydroxide (NaOH; 98%) powder and acetic acid (99.5%) were purchased from Samchun Chemicals, Inc. (Seoul, Republic of Korea). NaOH was dissolved in distilled water before use. Acetic acid was used without further treatment.

One-pot alkali hydrothermal treatment and ball milling equipment

The one-pot alkali hydrothermal treatment and ball milling equipment comprised three sections: supply, reaction, and collection (Fig. 1).

Rice husk was fed to the feed hopper and continuously supplied to the reactor via a screw. The rice husk feeding rate was controlled by changing the screw velocity, which determines the residence time of a sample in the reactor. The reaction section comprised a pulverizing ball mill and high-temperature reactor. The reactor had a volume

of 30 L. It was equipped with a rotating impeller to move the grinding steel balls and a heater to regulate the reactor temperature. The reactor was filled with 7 L of 20-mm diameter grinding steel balls. The rice husk sample occupied a volume of 16 L, and the remaining space served as the headspace. The temperature inside the reactor was set to 80 °C. During the continuous rice husk supply, the NaOH solution was also continuously flowed into the reactor using a peristaltic pump. The rice husk slurry was continuously discharged from the reactor using a peristaltic pump. Si was leached from the rice husk into the liquid phase, which was separated by vacuum filtration using filter paper (Whatman No. 41, 20 µm, Maidston, UK) and a vacuum pump (VLP200-115, Thermo Fisher Scientific Co., Waltham, MA, USA). For long-term operation, the rice husk sample and alkali solvent were initially added to the reactor, which was heated to 80 °C and the impeller was slowly rotated. When the reactor temperature reached 80 °C, the sample was continuously supplied and discharged. The screen in the outlet had a hole with a diameter of 6 mm to prevent the discharge of the grinding balls and insufficient grinding of the rice husk. To measure the solid content, samples were collected at the outlet, and their total and dried slurry weights were measured. The solid content is the ratio of the weight of the dried slurry to that of the total slurry.

Size-controlled spherical silica particles were synthesized according to a method described in our previous study to verify the possibility of using silicate solutions in the synthesis of value-added materials [5]. Briefly, 0.4 g of polyethylene glycol (PEG) and acetic acid (5 mL) were mixed in 200 mL of the silicate solution obtained from the one-pot continuous process at room temperature. The solution was stirred at 300 rpm using an electronic overhead stirrer (MD 3060D; MTOPOS, Yangju, Korea) at room temperature. After the reaction, the precipitated silica was filtered and washed with distilled water, followed by calcination at 550 °C for 2 h.

Analytical methods

To measure the leached silica yield, acetic acid was added to precipitate silica. The pH of the liquid was adjusted to 7.0 and stirred at 300 rpm overnight. The precipitate was washed three times with distilled water at 4000 rpm for 10 min. The washed silica was dried at 80 °C overnight and then calcined at 900 °C for 2 h. The leached silica yield was calculated using Eq. (1).

$$\text{Silica yield (\%)} = \left[\frac{\text{weight of precipitated silica}}{\text{weight of silica in RH}} \right] \times 100 \quad (1)$$

The composition of the rice husk was analyzed using the National Renewable Energy Laboratory (NREL)

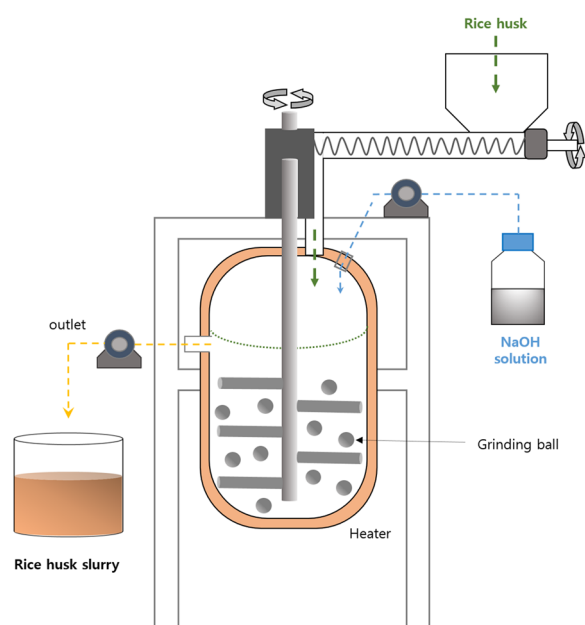


Fig. 1 Schematic of the one-pot alkali hydrothermal and ball milling continuous silica extraction process

procedure [11]. The inorganic composition was analyzed using inductively coupled plasma–optical emission spectrometry (ICP–OES; Optima 5300DV, PerkinElmer Co., Waltham, MA, USA). The crystallinity of the precipitated silica was analyzed using X-ray diffraction (XRD) using an X-ray diffractometer (D/Max 2500/PC, Rigaku Co., Tokyo, Japan). The energy consumption was calculated by integrating the recorded power over the operating time according to Eq. (2):

$$\text{Energy consumption} = \int_0^t \frac{(P_t - P_0)dt}{m}, \quad (2)$$

where P_t is the power (kW) consumed to dissolve silica at time t , P_0 is the power consumed during the initial operation under certain conditions, and m is the weight (kg) of silica obtained during time t . The consumed power was measured using an electronic power meter (LD3410DRM-040L; LS Electric Co., Republic of Korea).

A field-emission scanning electron microscopy (FE-SEM; JEOL, JSM-7000F, Japan, acceleration voltage: 10.0 kV) was used to analyze the morphology of the silica particles. SEM images were obtained without additional metal coating.

Results and discussion

Comparison of the silica extraction performance depending on residence time

In continuous chemical reaction processes, residence time is a key factor in determining the conversion efficiency and process capacity. The residence time of the rice husk in the reactor could be controlled by changing the flow rate in a continuous stirred tank reactor (CSTR). The change in conversion efficiency and process capacity depending on the residence time confirmed that this process can be stably operated and controlled. Therefore, three residence times were selected to investigate the performance of the continuous extraction process. Table 1 summarizes the performance of the continuous extraction process at the three resident times. As expected, the continuous extraction process exhibited different performances depending on the residence time. At a resident time of 50 min, the mean size of the rice husk particles

was 790 μm . As the residence time increased, the particle size decreased to 485 μm at 100 min and 200 μm at 150 min. The size of the rice husk particles prepared at a residence time of 150 min was 25% of that prepared at a residence time of 50 min. Increasing the residence time provided more time for the sample to be pulverized. Thus, smaller particle sizes were expected at longer residence times. Moreover, a longer residence time exposes the sample to chemical catalysis for a longer time. Therefore, higher silica yields were observed at longer resident times. The silica extraction yield was 86.0% at a resident time of 150 min, but it was only 52.8% and 69.1% at 50 and 100 min, respectively. Thus, relatively longer residence times lead to smaller particle sizes and longer chemical reaction times, causing synergistic effects and resulting in higher silica extraction yields. This study used a continuous process and thus its performance cannot be directly compared with batch-type reactions. But the silica extraction yields in this study are higher than the previously reported values of 72.4% (reaction time: 2 h) [12] and 79.9% (reaction time: 3 h) [9].

However, a longer residence time leads to a lower process capacity. Although a higher silica yield of 86.0% was obtained at 150 min, the silica production was only 2.22 kg day^{-1} . In contrast, at a resident time of 50 min, the silica production was 4.09 kg day^{-1} , although the silica extraction yield was low (52.8%). The quantity of silica produced is determined by both the silica yield and process capacity. The rice husk process capacities were 60.5, 30.2, and 20.2 kg day^{-1} for residence times of 50, 100, and 150 min, respectively. As shown above, a shorter residence time resulted in a lower silica yield, but more rice husk could be processed simultaneously compared to longer residence times. For example, a silica yield of only 52.8% was obtained at a residence time of 50 min but 60.5 kg day^{-1} rice husk could be processed, which is almost three times higher than that processed at 150 min. Thus, among the three residence times, the highest silica production was obtained at 50 min. The lower silica extraction yield at low residence times is owing to the insufficient pulverization and chemical reaction time. Using a high reaction temperature and solvent concentration may improve the silica yield, even at low residence times [9].

The continuous extraction device showed different energy consumptions depending on the residence time. Therefore, the energy consumed to produce 1 kg of silica was calculated and compared at the different residence times. In terms of energy consumption, a residence time of 150 min was the most energy-efficient condition, with an energy consumption of 47.4 MJ kg^{-1} . Although the highest silica production was observed at a residence time of 50 min, the energy consumption was

Table 1 Performance of the continuous extraction process at different residence times

Residence time (min)	50	100	150
Mean size of rice husk (μm)	790	485	200
Silica extraction yield (%)	52.8	69.1	86.0
Silica production (kg day^{-1})	4.09	2.67	2.22
Energy consumption (MJ kg^{-1})	51.6	47.7	47.4

51.6 MJ kg⁻¹, which is the highest among the three conditions. The residence time of 100 min exhibited a similar energy consumption (47.7 MJ kg⁻¹) to that of 150 min. In industrial applications, both energy consumption and silica production should be considered when selecting the optimum residence time. Although the residence time of 150 min showed the lowest energy consumption among the three conditions, it still required high energy. The energy consumption presented in this study is the energy consumed in the biorefinery to recover 1 kg of silica from rice husk. In addition to silica, carbohydrates could be separated and used to produce other value-added materials or energy [13, 14]. The energy consumption required to process 1 kg of rice husk was calculated for comparison with other studies. The energy consumption for processing 1 kg of rice husk was 3.49, 4.22, and 5.22 MJ kg⁻¹ at resident times of 50, 100, and 150 min, respectively. A previous study reported that the energy consumed to process 1 kg of wood was 1.98, 1.61, and 1.86 MJ kg⁻¹ for steam explosion, organosolv, and sulfite pretreatment, respectively [15]. The process developed in this study consumed more energy than those of Zhu and Pan. Recently, we demonstrated that the solid residue generated by the silica extraction process resulted in a 2.48-times higher biogas production than that obtained using untreated rice husk [13]. This indicates that the silica extraction process used in this study has the same effects as the lignocellulose pretreatment conducted to improve energy production. Although the energy consumption of the method used in this study was higher than that of their study, the developed method can provide both improved energy production and value-added silica particles, which should be considered in an economic analysis.

Long-term continuous extraction of silica

Stable operation is also an important factor in continuous processes. To verify the stability of the continuous silica extraction process, the solid content at the outlet and the silica extraction yield were measured for 150 h. Figure 2 shows the solid content at the outlet and the silica extraction yield after reaching steady-state.

A constant solid content in the reactor is essential for achieving a stable performance during continuous operation. If the discharge of liquid and solid from the reactor is unbalanced, the reaction conditions will change, and silica extraction will be unstable. The solid content was approximately 13% throughout the operation. This indicates that the rice husk sample was mixed well in the reactor and maintained the same solid-to-liquid ratio during operation. Moreover, the silica extraction yield was constant at approximately 86.0% for 150 h. Because the continuous silica extraction reactor maintained a

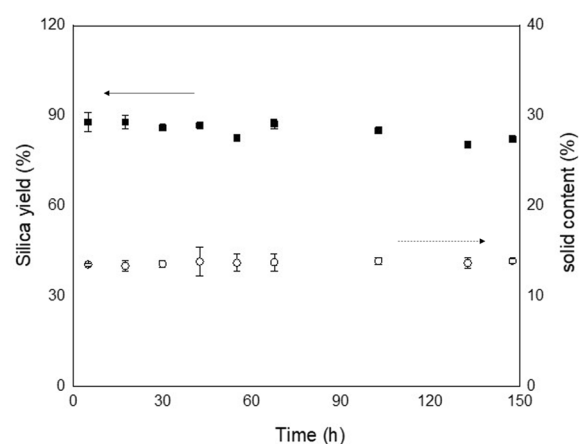


Fig. 2 Silica extraction yield and solid content during long-term operation

constant temperature and the same reaction conditions with a constant solid content, the silica extraction also remained constant during the operation. The system was operated for 150 h after reaching a steady state. During the operation, 126 kg of rice husk was processed and 13.9 kg of silica was obtained. The constant silica yield obtained during the long-term operation indicates that the continuous process used in this study can operate steadily for an extended period.

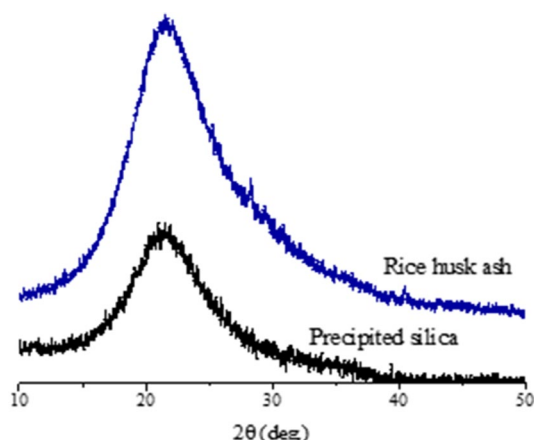
Characteristics of the extracted silica particles

The characterization of the precipitated silica was performed. The precipitated silica has a purity of 99.1 wt% (Table 2). Compared to the rice husk ash, the content of three elements, Ca, Mg, and K, were considerably reduced in the silica particles obtained during long-term operation. Thus, the one-pot alkali hydrothermal and ball milling method used in this study effectively removed these three elements. In contrast, the Na content increased from 0.08 to 0.35 wt% owing to the relative increase caused by the removal of other metallic impurities. Therefore, the one-pot continuous reaction was more effective at removing impurities than the two-stage continuous reaction used in our previous study [9]. In the two-stage continuous process, 98.5 wt% of silica was obtained. The higher purity of silica obtained in the current study may be owing to the combined effects of the larger scale of the reaction and the simultaneous alkali hydrothermal treatment and ball milling processes.

The structure and purity of the precipitated silica obtained from the continuous extraction process were verified by XRD, as shown in Fig. 3. A characteristic broad peak centered at a 2 θ value of approximately 22.7° was observed, indicating the amorphous nature of the rice husk ash and the silica particles in the precipitated

Table 2 Inorganic composition of the precipitated silica obtained during the long-term operation experiment and rice husk ash

	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
Precipitated silica (wt%)	99.1	0.02	0.02	0.01	0.35	0.04
Rice husk ash (wt%)	93.1	0.05	1.52	0.65	0.08	0.84

**Fig. 3** X-ray diffraction patterns of the precipitated silica and rice husk ash

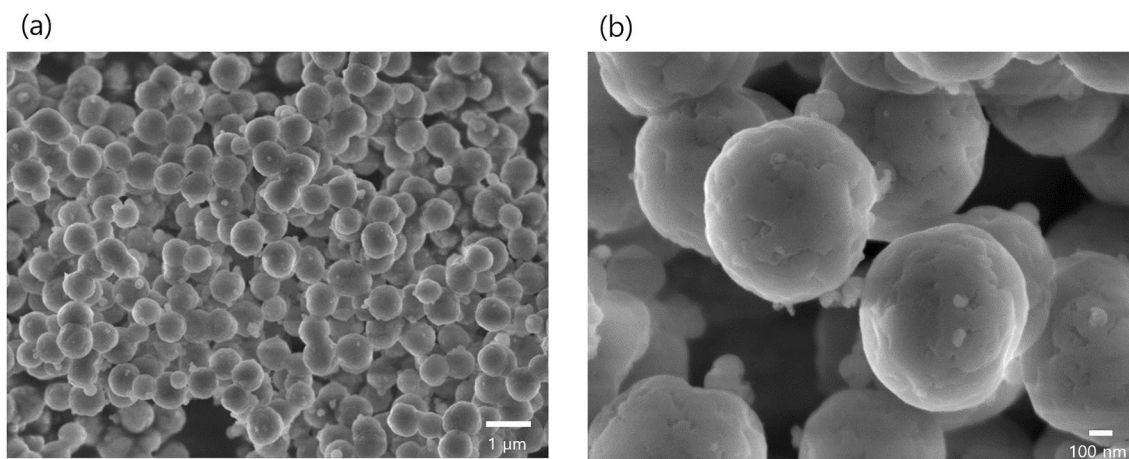
silica obtained by the continuous extraction process. This indicates that the continuous extraction process did not change the crystallinity of silica. A previous study also reported that the crystallinity of silica is determined by the calcination temperature applied and not by the chemical treatments utilized [16]. The amorphous nature of rice husk-derived silica has been reported elsewhere [4–9, 16]. No other peaks were observed in the XRD pattern, indicating the absence of impurities.

To investigate the feasibility of using the silicate solution obtained in the one-pot continuous reaction to synthesize value-added silica particles, size-controlled spherical silica particles were synthesized according to our previous study [5]. As shown in Fig. 4, the silicate solution obtained via the one-pot extraction was successfully used to synthesize uniform spherical silica particles, confirming that the silicate solution produced in this study can be easily applied to established silica synthesis methods.

The application of the silicate solution obtained by the continuous silica extraction process was investigated. However, carbohydrates remained in the solid residue and its application in the synthesis of a value-added material should be investigated in the future.

Conclusions

The successful utilization of rice husk as a renewable raw material requires an ideal biorefinery process. In this study, a one-pot continuous silica extraction process involving the alkali hydrothermal treatment and ball milling of rice husk was developed. This continuous process showed different performances depending on the residence time, which indicated that the process could be controlled by changing the residence time. Among the three residence times investigated, the highest silica production was achieved at a residence time of 50 min. However, the residence times of 100 and 150 min exhibited

**Fig. 4** (a, b) SEM images of size controlled silica synthesized using silicate solution obtained from the one-pot continuous extraction process

similar energy consumptions (47.7 and 47.4 MJ kg⁻¹, respectively), which were better than that observed at a residence time of 50 min (51.6 MJ kg⁻¹). In addition, it was confirmed that the one-pot continuous process could be operated stably in terms of the solid content and silica extraction yield for 150 h. The silica extracted by the one-pot continuous process had a high purity and an amorphous structure. Moreover, the silicate solution produced in this study was successfully used as a raw material for the synthesis of size-controlled silica particles. Thus, this study presents a novel and effective method for the extraction of silica from rice husk, which advances the valorization of rice husk. Future research should include the integrated utilization of carbohydrates and the silicate solution separated from the one-pot continuous process as raw materials for the synthesis of value-added materials to maximize the utilization of rice husk.

Abbreviations

NaOH	Sodium hydroxide
PEG	Polyethylene glycol
NREL	National Renewable Energy Laboratory
XRD	X-ray diffraction
CSTR	Continuous stirred tank reactor

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Not applicable.

Author contributions

JYP, writing-original draft, methodology, investigation; YMG, sample analysis; JC, silica particle synthesis; BS, validation, supervision; JHL, writing-review and editing, supervision, project administration, funding acquisition. All authors have read and agreed to the published version of the manuscript.

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Availability of data and materials

Not applicable.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interest.

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