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Original Article

Amorphous silica production from Colombian rice husk: demonstration in scaled-up process Products

Obtención de sílice amorfa a partir de cascarilla de arroz colombiana: demostración en proceso escalado

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Abstract

Introduction: the agroindustry generates significant waste, posing environmental, health, and economic challenges. Among these, rice husk, a byproduct of the food industry, stands out due to its potential as a source of silicon. Due to its silicon content, rice husk offers a unique opportunity for sustainable energy production and the extraction of high-value products, such as amorphous silicon dioxide (SiO2). However, optimizing processes for its efficient conversion remains a challenge.
Objective: the aim of this study was to optimize the nitric acid concentration for the pretreatment of Colombian rice husk in order to produce high-purity amorphous SiO2 and demonstrate the feasibility of scaling up the process.
Methods: a two-stage process was developed, which involved treating rice husk with nitric acid, followed by calcination at 620 °C. The nitric acid concentration was optimized to achieve the highest SiO2 purity. Material characterization was performed using thermogravimetric analysis (TGA), X-ray diffraction (XRD), X-ray fluorescence (XRF), and nitrogen adsorption-desorption. To assess the scalability of the process, the treatment was replicated on a larger scale using the optimized acid concentration.
Results: the optimized process using a nitric acid concentration of 0.2 M yielded amorphous SiO2 with a purity of 94.9% and a surface area of 298 m²/g. When scaled up, the process achieved SiO2 with a purity of 95.5%, confirming the feasibility of the methodology for industrial applications.
Conclusions: the treatment of rice husk with nitric acid followed by calcination proves to be an effective and scalable approach for producing high-purity amorphous SiO2. This process not only holds potential for industrial applications but also provides a sustainable solution for valorizing agroindustrial waste, contributing to the circular economy.

Keywords: silicon oxide, Rice husk, Materials characterization, Upscaling process.

Resumen

Introducción: la agroindustria produce grandes cantidades de desechos, lo que genera retos ambientales, de salud y económicos. Entre estos, la cascarilla de arroz, un residuo de la industria alimentaria, se destaca por su potencial como fuente de silicio. Gracias a su contenido de silicio, la cascarilla de arroz ofrece una oportunidad única para la producción de energía sostenible y la obtención de productos de alto valor agregado, como el óxido de silicio amorfo (SiO2). Sin embargo, la optimización de los procesos para su conversión eficiente sigue siendo un desafío..
Objetivo: optimizar la concentración de ácido nítrico para el pretratamiento de la cascarilla de arroz colombiana, con el fin de producir SiO2 amorfo de alta pureza, y demostrar la viabilidad de este proceso a escala mayor.
Métodos: se desarrolló un proceso en dos etapas que incluyó el tratamiento de la cascarilla de arroz con ácido nítrico, seguido de una calcinación a 620 °C. La concentración de ácido nítrico se optimizó para obtener la mayor pureza de SiO2. La caracterización del material se realizó mediante análisis termogravimétrico (TGA), difracción de rayos X (XRD), fluorescencia de rayos X (XRF) y adsorción-desorción de nitrógeno. Para evaluar la escalabilidad del proceso, se replicó el tratamiento en una escala mayor utilizando la concentración óptima de ácido.
Resultados: el proceso optimizado utilizando una concentración de ácido nítrico de 0.2 M produjo un SiO2 amorfo con una pureza del 94.9 % y un área superficial de 298 m^2/g. Al escalar el proceso, se logró un SiO2 con una pureza de 95.5 %, confirmando la viabilidad de la metodología para aplicaciones industriales.
Conclusiones: el tratamiento de cascarilla de arroz con ácido nítrico, seguido de calcinación, demuestra ser un enfoque efectivo y escalable para la obtención de SiO2 amorfo de alta pureza. Este proceso no solo tiene aplicaciones industriales potenciales, sino que también proporciona una solución sostenible para la valorización de los desechos agroindustriales, contribuyendo a la economía circular.

Palabras clave: óxido de silicio, cascarilla de arroz, caracterización de materiales, proceso de escalamiento.

Why was it done?
This work was done because we were exploring the possibilities to obtain value added products from rice husks. Among the possibilities there was the route to obtain carbonaceous materials using pyrolysis, or silicon rich materials by using thermochemical process. We decided to try the second one in order to obtain amorphous silicon oxide. Following this route we scale-up the process using nitric acid, which is commercially available in colombian context.

What were the most relevant results?
We obtained amorphous silicon with a purity >95% using a thermochemical process. In this process we found that using a nitric acid concentration as low as 0,2M was enoguh to reach that purity. Also, the scale-up process was succesfully implemented by processing 2 Kg of rice husk, leading to an amorphous silicon of >95% and a surface area >290 m2/g

What do these results provide?
The results of this study demonstrate the feasibility of using rice husks to produce high-purity amorphous silicon oxide through a thermochemical process with nitric acid. Achieving over 95% purity at a low concentration of 0.2 M indicates both efficiency and cost-effectiveness. The successful scale-up to process 2 kg of rice husks validates its industrial applicability. Additionally, the resulting material boasts a high surface area of over 290 m^2/g, enhancing its potential for various applications. Overall, this research highlights the sustainable valorization of rice husks as a valuable resource.

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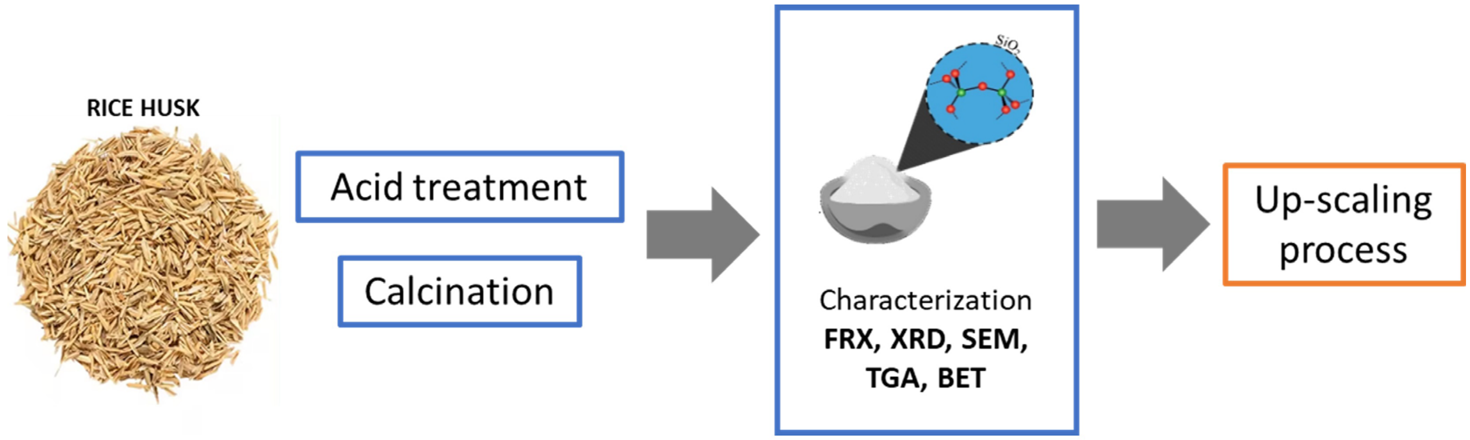
Graphical Abstract



Introduction

Agroindustry, the integration of agriculture and industry for food production or raw materials, generates significant waste that cause environmental, health, and economic challenges. Issues include greenhouse gas emissions, climate change, water source contamination, and respiratory diseases from air pollution. However, these biomass wastes have untapped potential for energy production or value-added products (1) and recent interest has focused on developing technologies for their biological, chemical, or thermal valorization, offering low-cost and readily available raw materials (2). This utilization is crucial for making industrial activity more sustainable.

In this context, rice is a staple food produced worldwide, that yields rice husks as a by-product, constituting 20 % of the total product and contains silicon in form of valuable silica (SiO_2) (3). With global rice production exceeding 500 million tons annually (4), the abundance of rice husk presents an attractive opportunity for sustainable production of silicon-based materials or composites. Since 1980s, various applications have been explored, including manufacturing cement and rubber, extruding polymers with natural fibers, producing insulating materials, and using rice husks as fuel for drying rice and obtaining energy for other purposes (5).

Recent studies have proposed sustainable methods for environmentally friendly production of silicon oxide (SiO_2), gaining significance in both scientific and industrial applications (6, 7). Chemical treatments, often involving pre-treatments in basic and acid media, are frequently employed to recover SiO_2 from rice husks. These pre-treatments typically remove impurities and dissolves undesired elements in the husks. Then, by conducting calcination in oxidizing atmospheres at temperatures between 500 and 900 ºC, the organic material is eliminated yielding a high-purity silica with an amorphous or crystalline structure depending on the calcination temperature (8, 9). This method exhibits a well-established result, which makes rice husks a viable alternative source for industrial applications of silicon oxide. Despite the well-establish method for obtaining silicon oxide from rice husk, the use of some strong acids (i.e. hydrochloric acid and sulphuric acid), is restricted in many countries. So, for a potential scale-up of the process it is necessary to use highly commercially available acid, such as nitric acid.

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In this work, a simple methodology was implemented for obtaining amorphous silicon oxide using Colombian rice husk as a source. By using the methodology proposed, it was optimized the concentration of highly available commercial nitric acid for the pretreatment of rice husk and the obtained materials were characterized after calcination. It was found that a concentration of acid of 0.2 M was enough to reach an optimized silicon oxide content. So, a scaling-up process was undergoing to treat 2 kg of rice husk to produce an amorphous silicon oxide with an 95.5 % purity and 298 m^2/g of surface area.

Methodology

Rice husk (purchased in a local agricultural store), nitric acid (50% w/w) and deionized water, were used for the process. To produce the amorphous silicon oxides, the rice husks were washed using different nitric acidic solutions (0.2 M, 0.5 M, 1.0 and 2.0 M) for two hours employing a magnetic stirrer. For all the experiments, it was used 25 mL of acidic solution per gram of rice husk. Subsequently, the treated husks were recovered by filtration and washed with deionized water until neutral pH. Finally, the washed husks were calcined using a muffle, at a heating ramp of 10 °/min up to 620 °C, for three hours. Figure 1 depicts the process to obtain amorphous silicon oxide.

The rice husk was characterized using thermogravimetric analyses (TGA) using a TGA 5500 equipment from TA Instruments. The obtained amorphous SiO_2 was characterized using scanning electron microscopy (SEM) by using an JEOL JSM 6490 LV equipment. Fluorescence X ray (FRX) analyses were carried out using a dispersive wavelength equipment from PANAlytical reference Zetium 4kW. X ray diffraction (XRD) measurements were carried out using an XPert PANalytical Empyrean Serie II. Finally, the surface area of the materials was determined by nitrogen adsorption-desorption isotherms using Micromeritics, ASAP 2020 PLUS Instrument.

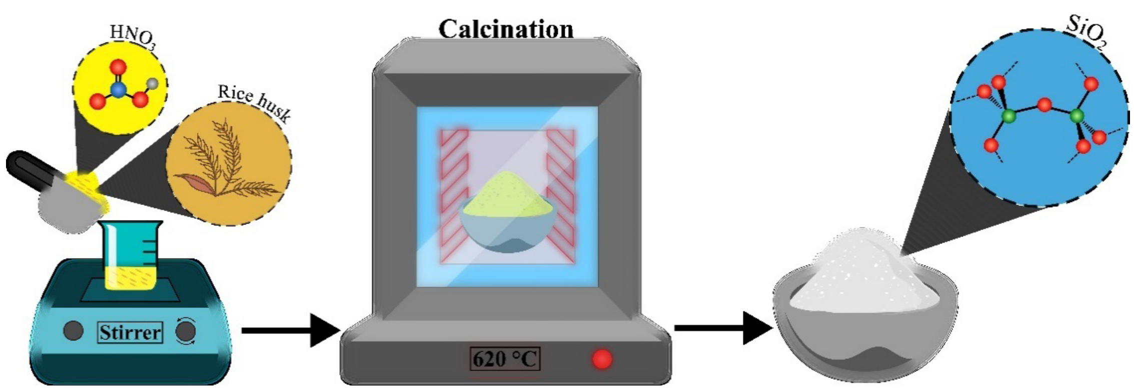

Figure 1. Schematic representation of the proposed methodology for the treatment of rice husks.

Based on the obtained results at lab-scale, a scaling-up procedure was conducted employing an 80 liters capacity mixer. The process employed 2 kg of rice husk and 50 L of 0.2 M HNO_3 aqueous solution. The mix was stirred using an industrial mixer by a determined time. The treated rice husk was recovered by filtration and washed with water until a neutral pH was obtained. Finally, the obtained husk was calcined to obtain the amorphous silicon oxide.

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Results and discussion

In order to evaluate the effect of the concentration of nitric acid (HNO_3) used to wash the husk, thermogravimetric analyses were carried out to determine the amount of ash in each of the materials. Figure 2 shows the TGA analyses of the rice husks after each acid treatment. It can be observed that the decomposition profile of the materials does not change significantly after the treatment. In general terms, it was found that an increasing trend in the ash content by increasing the concentration of the acid treatment. So, for an acid treatment of 2.0 M it was found a final percentage of 16.5 % while for an acid treatment of 0.2 M the final weight percentage was 14,4 %. This can be attributed to the inherent heterogeneity of the organic matter and to the removal of impurities with the acid treatment, resulting in a slight increase in the final percentage of ash obtained.

On the other hand, the thermal profiles showed a first weight loss in the range 25 – 100 °C which corresponds to the loss of humidity. The subsequent weight loss between 240 and 343 °C is related to the decomposition of the cellulose and hemicellulose present in the husks. Then, a third zone is observed between 360 and 620 °C and is attributed to the decomposition of lignin and the final formation of ashes (10). The last thermal decomposition (360 – 620 °C) of the non-treated acid rice husk differs from the treated ones. So, thermal decomposition occurs rapidly for the non-treated rice husk. In this regard, acid treatment eliminates primarily hemicellulose (11) more than lignin, so the treated samples contain more lignin compared to the raw sample. Therefore, the higher thermal stability of treated samples could be attributed to a higher percentage of lignin.

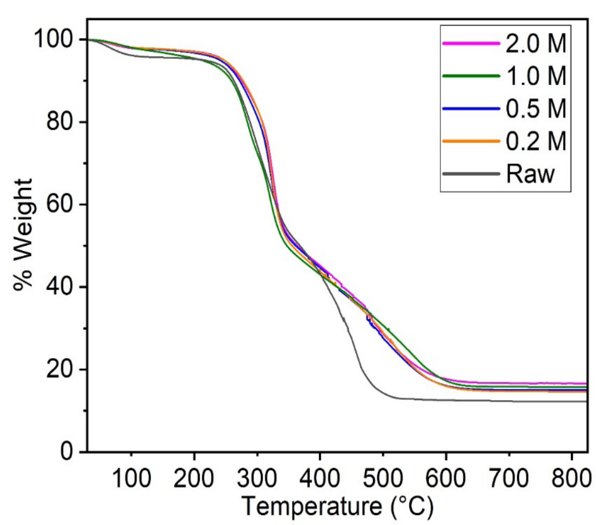

Figure 2. TGA profiles obtained for the rice husks

In order to confirm the amorphous character of silica obtained, X-ray diffraction analyses were performed (Figure 3) for non-treated sample, 0.2 M treated sample, and the one treated with the harsh condition (2.0 M). The XRD results show that the obtained materials present an amorphous crystalline structure corresponding to SiO_2. In addition, there is not relationship between the ordering of the structure and the concentration of HNO_3 used for the treatment, which is consistent with the findings of other authors (12, 13, 14).

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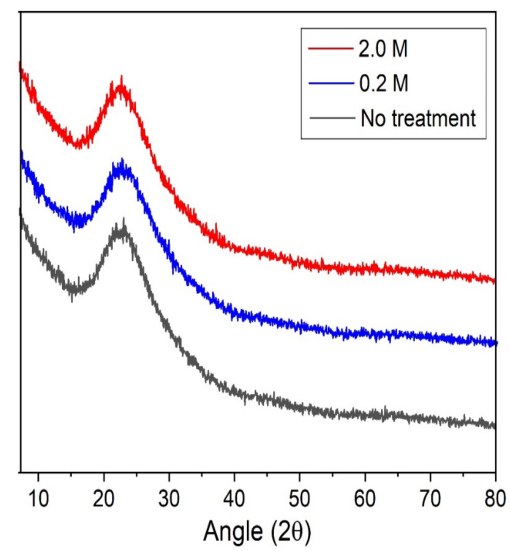

Figure 3. XRD patterns of the silica obtained.

Likewise, the content of SiO_2 was determined by XRF as depicted in Figure 4. The SiO_2 content varies from 90.0 to 94.9 % within the samples, as shown in Figure 4A. In general terms, the use of an acid treatment prior to calcination of the rice husk results in increasing of the SiO_2 content due to the leaching effect that acid has over other metal oxides (Figure 4B) (15, 16).

It was found that there is no significant increase of the SiO_2 content by increasing the concentration of nitric acid beyond 0.2 M. In this regard, the SiO_2 content in the sample treated with 0.2 M was 94.7 % while the treated with 2.0 M was 94.9 %. Within this context, it can be found that the concentration of acidic solutions (i.e. HCl, HNO_3 and H_2SO_4) for the treatment of rice husk varies between 0.01 M and 3.0 M depending on the type of rice husk and pretreatment prior to calcination (17, 18, 19). This broad range found for the acid concentrations is primarily due to the presence of potassium, magnesium and calcium oxides in rice husk derived from the type of fertilizer and soil used in rice plantations (20, 21). For the case of Colombian rice husk, the most common fertilizer used is KCl (22) so this is the primarily compound that need to be removed from the rice husk. This agrees with the large content of potassium found in the non-treated ash, as shown in Figure 4B.

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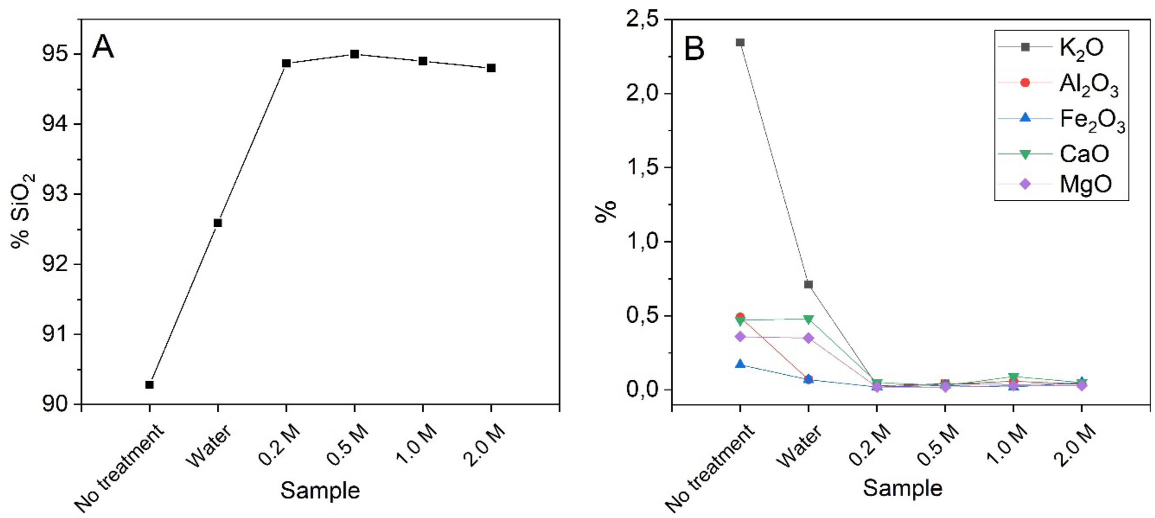

Figure 4. XRF results in terms of silicon content (A) and other metal oxides (B).

On the other hand, the surface area of the materials was obtained by nitrogen adsorption-desorption. Results are shown in Figure 5A. Accordingly, a surface area of 81 m^2/g was obtained for the sample without any treatment while for treated ashes the values varied from 299 to 338 m^2/g, depending on the concentration of HNO_3 used for pretreatment. It was noted that the acid treatment had a large influence on the surface area of the materials obtained. This is correlated to the presence of potassium in the samples. As previously discussed, the husk contains a substantial amount of potassium, which can dissociate at low temperatures to produce elemental potassium. This process causes surface melting, resulting in the entrapment of carbon within the melt. As a result, direct contact with air is eliminated, preventing oxidation during subsequent calcination. Therefore, the high K_2O content in the untreated rice husk sample promotes the formation of sintered particles and hinders the creation of a highly porous structure (23, 24). Also, the formation of a porous structure due to calcination, promoted the high surface area as shown in SEM analyses (Figure 5B).

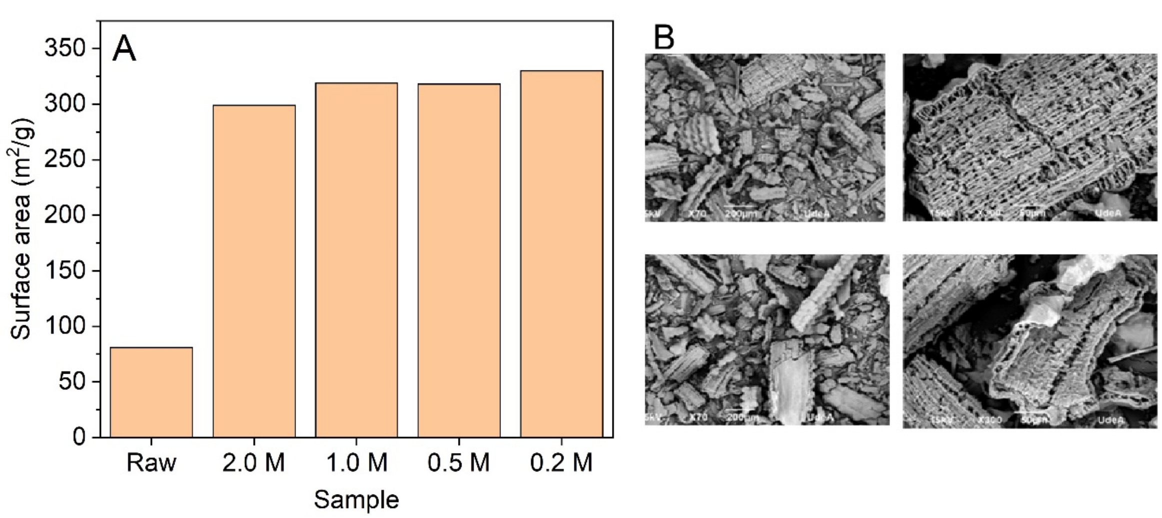

Figure 5. BET surface areas of samples (A) and SEM images of obtained ash (B)

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Considering the results presented before a scaling-up process was done. For doing so an 80 liters capacity mixer was used for processing 2 kg of rice husk using a solution 0.2 M HNO_3, as shown in Figure 6A. To evaluate the effect of processing time in the silicon content, a sample was taken from the tank every 2 hours, further calcined, and analyzed using FRX. The results are shown in Figure 6B. At a processing time of 2 hours a content of 95.5 % of SiO_2 was found within the sample. In contrast, at 6 hours of processing time the SiO_2 content reach 95.9%. So, there is no major influence of processing time in SiO_2 content after two hours of treatment. Also, a slight increase in SiO_2 content was found in the ashes using the scaling-up process (95.5 %), in comparison to the one obtained in the lab (94.9 %). This is probably due to the high torque and strength of the stirrer used in the tank (Figure 6A) that allows the rupture of the husks and improves the penetration of the acid. Also, it was found that an amorphous silicon oxide was obtained (Figure 6C) with a surface area of 280 m^2/g.

These results demonstrate that the thermochemical process proposed for obtaining amorphous silica from Colombian rice husk is feasible using nitric acid of 0.2 M, rendering its potential for a scalable process.

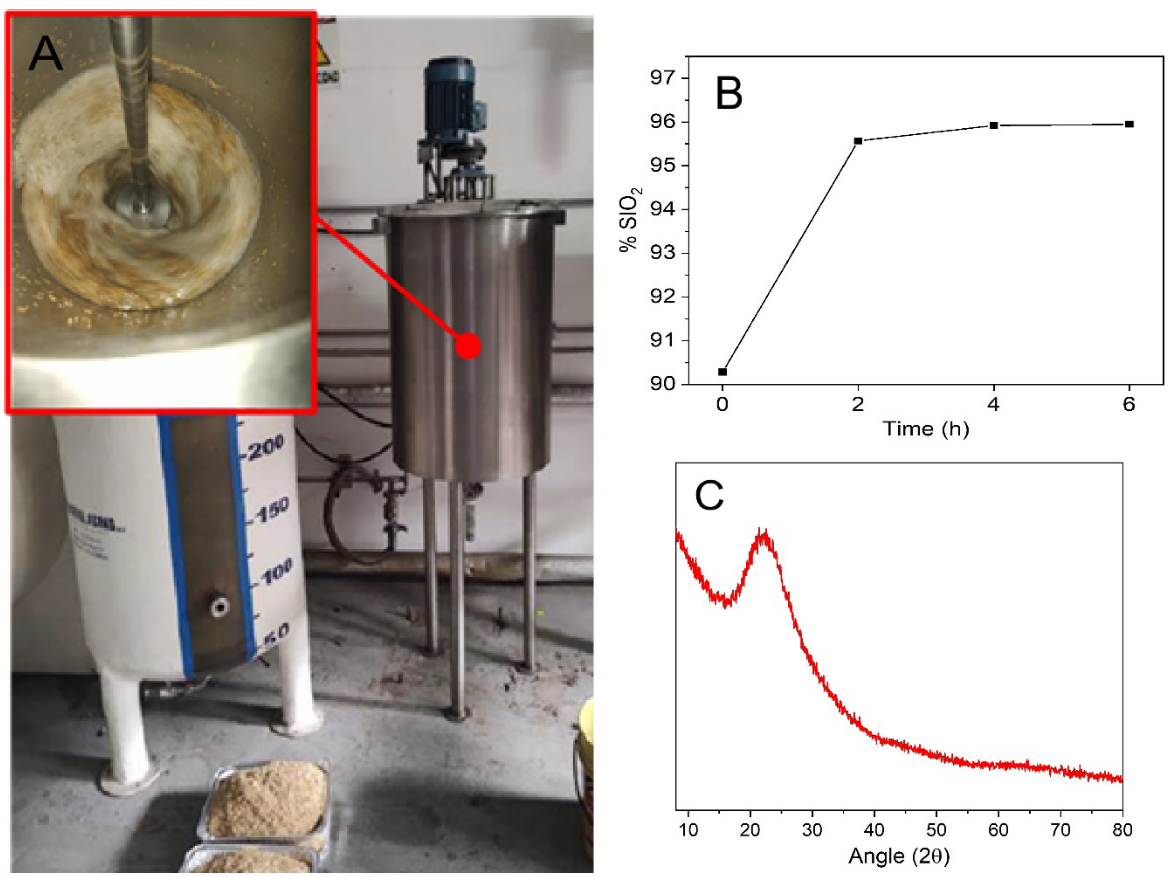

Figure 6. Upscaling process for silicon oxide obtaining (A), Silicon oxide content of resulted materials (B), XRD pattern of obtained material (C).

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Conclusions

This study evaluated the effects of varying concentrations of HNO_3 used to wash rice husk on the thermal and structural properties of the resulting materials. TGA analysis showed that increasing the concentration of nitric acid led to a higher ash content, revealing the removal of impurities and a slight increase in the final percentage of ash obtained.

XRD analysis confirmed that the silica obtained from both, treated and untreated rice husk samples, exhibited an amorphous crystalline structure, with no significant relationship between the degree of ordering and the concentration of HNO_3 used. XRF analysis demonstrated that the SiO_2 content varied between 90.0 % and 94.9 %, with no significant increase beyond a 0.2 M HNO_3 concentration. The acid treatment effectively increased the SiO_2 content by leaching other metal oxides, highlighting the potential for optimizing the concentration for maximum efficiency.

Nitrogen adsorption-desorption results indicated that the surface area of the obtained silicon oxides significantly increased with the acid treatment, ranging from 299 to 338 m²/g, compared to 81 m²/g for untreated samples. This increase is attributed to the reduction of potassium-induced sintering and the formation of a porous structure during calcination, as confirmed by SEM analyses.

A scaling-up process using an 80-liter capacity mixer and 0.2 M HNO_3 was successfully implemented, demonstrating that a 2-hour processing time was sufficient to achieve optimum SiO_2 content. The scaled-up process produced amorphous silica with a slightly higher SiO_2 content (95.5 %) and a surface area of 280 m²/g, validating the feasibility and scalability of the thermochemical process.

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CRediT authorship contribution statement

Conceptualization - Ideas: Daniela Jaramillo, Santiago Mesa. Data Curation: Santiago Mesa Espinal. Formal analysis: Santiago Mesa, Daniela Jaramillo, Laura C. Urán. Acquisition of funding: Santiago Mesa. Research: Santiago Mesa, Daniela Jaramillo, Carlos Vélez. Methodology: Daniela Jaramillo. Project Management: Santiago Mesa, Laura Urán. Resources: Santiago Mesa. Supervision: Laura Urán, Carlos Vélez. Validation: Santiago Mesa. Visualization - Preparation: Santiago Mesa, Daniela Jaramillo. Writing - original draft - Preparation: Daniela Jaramillo. Writing - revision and editing - Preparation: Santiago Mesa, Daniela Jaramillo.

Ethical implications

The authors do not have any type of ethical involvement that should be declared in the writing and publication of this article.

Conflict of interest

The autors no declare.

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