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A Study of the Optimal Conditions for Extracting and Precipitating Silica from Rice Husk Using the Hydrothermal Method in a Base Medium

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Abstract

This research investigated the extraction and precipitation methods of silica from rice husk using hydrothermal treatment under basic conditions. It was observed that by subjecting raw rice husk and black rice husk ash to burnt at a temperature of 700°C for 6 hr raw rice husk yielded 10.68%, while black rice husk yielded 85.40%. The optimal condition for extracting silica is 1 molar of sodium hydroxide at a temperature of 100°C for 6 hr. Silica extracted from raw materials that have undergone acid pretreatment yields a higher quantity compared to silica from untreated raw materials. However, the raw rice husk, burnt raw rice husk, black rice husk ash and burnt black rice husk ash have silica % of 16.20, 77.60, 63.10 and 89.0, respectively. When the extracted silica was analyzed for its physical characteristics using an inverted microscope, it was observed that silica subjected to acid pretreatment exhibits uniformly sized particles. The examination of particle size using the extraction method revealed that the silica particles were smaller than 53 µm and when all extracted silica was analyzed for functional groups using the FT-IR technique, the siloxane group (Si-O-Si) was found in the wavenumber range of 1,090-801 cm^{-1}. Additionally, the hydroxyl group (-OH) was observed at the wavenumber of 3,400 cm^{-1}. After conducting Brunauer–Emmett–Teller Analysis (BET analysis) on silica obtained from burnt rice husk and burnt black rice husk ash, both untreated and treated with HCl, it was found that the pore diameter of the extracted silica ranged from 8.14 to 19.15 nm. This suggests that the silica possesses mesoporous characteristics. Furthermore, the acid-leached silica exhibited a decrease in particle size and an increase in surface area. Specifically, the silica derived from burnt rice husk and treated with HCl demonstrated particle size and surface area values that closely resembled those of commercial-grade silica.

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When studying the effectiveness of silica in adsorbing methylene blue, the findings showed that the extracted silica demonstrates better adsorption capability for methy lene blue compared to commercial silica. The adsorption values ranged from 1302.49 to 1706.35 mg MB/g, representing 65.78-86.17%. From the investigation of the isotherm for methylene blue adsorption with the extracted silica, it is evident that the adsorption conforms to Freundlich model, indicating a multilayer adsorption behaviour. The method of extracting and precipitating silica through hydrothermal treatment under basic conditions proves to be an effective approach for preparing micro-sized silica particles.

Introduction

Rice husk is a waste material from the rice milling process. It is a residual material with potential agricultural uses, such as biofuel production, electricity generation, animal feed and soil improvement. However, there is still a considerable amount of rice husk that needs to be disposed of, either through burial or incineration. This leads to significant environmental pollution issues.

The chemical components and structure of rice husk consist of cellulose, lignin, and organic compounds. The organic components in rice husk include silicon compounds, constituting 95% by weight (Chumee, 2011; Jarupan, 2018). When rice husk is incinerated to produce biofuel, it transforms into ash, and the resulting silica content was found to be 91.05% (Jarupan, 2018). Therefore, the results of the prior research have led to the idea of extracting silica from rice husk ash. The extracted silica is intended to be utilized as a substitute for commercially available silica, aiming to reduce dependence on imported silica from foreign sources.

Silica, or silicon dioxide (SiO_2), is a compound of silicon and oxygen with an amorphous, colorless or white powdery appearance. It is odorless and tasteless, commonly found in soil and rocks (Pengthamkeerati et al., 2018). The synthesis of silica from rice husk can be achieved through various methods, including the sol-gel process, flame spray pyrolysis, hydrothermal method and precipitation method. The synthesis process involves using raw rice husk or rice husk ash obtained through incineration. After the removal of impurities and organic carbon, silica is obtained and the resulting silica is approximately 91.05% pure. The synthesized silica exhibits porous characteristics and high surface area, making it suitable for various industrial applications such as pharmaceuticals, cosmetics, abrasives, moisture absorbents, thickening agents, coatings and water-absorbent materials in wastewater treatment plants, among many other usages (Jarupan, 2018). The hydrothermal process is an efficient and environmentally friendly method to extract silica from rice husk. The extracted silica has a high purity, surface area and porosity (Nzereogu, et al. 2023).

In this research, the objectives were to explore suitable conditions for separating and precipitating silica from rice husk and black rice husk ash using the hydrothermal method in a basic environment. The study aims to investigate the efficiency of the separation method and the precipitation of various silica materials. Additionally, the research examined the physical and chemical properties of the extracted silica and assess its effectiveness in adsorbing the dye methylene blue.

Materials and methods

1. Materials

The collection of samples was gathered from two types. The raw rice husks were used as samples. The raw rice husks (Kao Hom Mali Khoko 6) were collected from Yasothon Province and the black rice husk ash samples were collected from Suphanburi Province. The chemicals used for extracting silica from both rice husks and black rice husk ash included hydrochloric acid (HCl) (AR grade, brand QReC, New Zealand), sodium hydroxide (AR grade, brand Univer, Austria) and silver nitrate (AR grade, brand POCH, Poland). Chemicals used for testing the properties of silica include methylene blue (AR grade, brand BDH, England). Commercial silica used for comparison was silica gel 60 with particle size less than 0.063 mm, product code 1.07729.1000, (AR grade, brand Merck, Germany.)

2. Sample preparation without acid leaching

For preparation of the raw rice husk samples, first they were cleaned by washing with distilled water to remove impurities and then oven-dried. The dried samples were stored in sealed bags. As for preparing black rice husk ash samples, they were left to cool after being oven-dried, then grounded into a fine powder. The powdered samples were stored in sealed bags. Subsequently, 5 g of each sample type were weighed and poured into crucibles without sealing the lids. The crucibles were then placed in a controlled temperature furnace at 700°C for 6 hr. After cooling in the furnace, the samples were ground into a fine powder, re-weighed and the weight percentage of the yield was calculated. The resulting samples were stored in sealed bags. The samples are shown in Fig. 1. In preliminary studies, the burning temperature of raw rice husk and black rice husk ash in the range of 600 - 900°C took 6 hr. It was found that when the temperature was 600°C, the resulting rice husk ash had a fine powder appearance, gray with some black and when subjected to silica extraction, approximately 10-20% silica was obtained. However, as the temperature increased in the range of 700-900°C, the rice husk ash appearance became grayish-white and when subjected to silica extraction, approximately 77-80% silica was obtained from raw rice husk, while black rice husk ash yielded approximately 89-91% silica. Therefore, since the quantities of silica obtained were similar, the researchers chose to burn at a temperature of 700°C to conserve energy during burning.

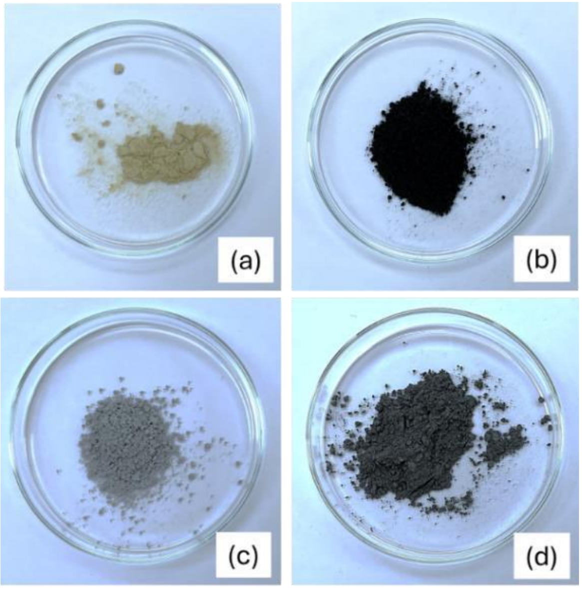


Fig. 1 Samples a) raw rice husk b) black rice husk ash c) burnt rice husk and d) burnt black rice husk ash

3. Sample preparation with hydrochloric acid extraction

The preparation began with weighing 5.00 g of prepared raw rice husk and black rice husk ash samples. The acid extraction was performed using HCl with a concentration of 1 molar, at a ratio of 1:10 (sample to acid) at room temperature, 60°C and 100°C. The extraction process took 1 hr and the samples were left to cool. Subsequently, the samples were washed with distilled water until the pH was 7. The samples were then filtered, dried and the remaining weight was recorded.

4. Study to determine optimal conditions for silica extraction and precipitation

Silica extraction and precipitation begins by weighing 1.00 g of prepared samples and poured into 125 ml conical flasks. Then, a 1 molar solution of sodium hydroxide was added, maintaining a 1:10 ratio between the sample and sodium hydroxide solution. The flasks were sealed with rubber stoppers containing a thermometer. The mixtures were heated to room temperature, 60°C and 100°C for 1 hr each. Then they were allowed to cool. After cooling they were filtered and separation of the substances was placed into two parts.

Part 1: The solid part on the filter paper was dried and weighed to determine the efficiency of silica extraction using the following equation 1:

$$\text{\% of Silica extraction efficiency} = \frac{(\text{Initial sample weight} - \text{Remaining sample weight})}{\text{Initial sample weight}} x\ 100 \quad (1)$$

Part 2: The obtained solution was adjusted to a pH of 7 and left for 24 hr. The upper portion on the filter paper was then dried and its weight was measured to determine the efficiency of silica precipitation using the following equation 2:

$$\text{\% of Silica precipitation efficiency} = \frac{\text{Weight of obtained solid from precipitation}}{\text{Intial sample weight}} x100 \quad (2)$$

Consideration for selecting suitable conditions for silica extraction and precipitation was based on achieving the minimum amount of remaining solid after separation and the maximum amount of solid obtained after precipitation. The results are reported in percentage units (Pengthamkeerati et al., 2018).

5. Study of the physical properties of extracted silica

The prepared rice husk samples and the extracted silica were sieved using sieves No.100 (150 µm), No.120 (125 µm) and No.270 (53 µm) in sequence, utilizing a temperature-uncontrolled shaking machine, model KS 501, by STP, Germany. Observation of the quantity of silica passing through each sieve to determine the size of the prepared clay and the extracted silica. Additionally, the extracted silica was placed on a slide, approximately 0.1-0.2 mg, with water on the slide's surface. Then, the sample was spread evenly and covered with a glass coverslip. The sample was examined using an inverted microscope (MBL3200 model by Kruss, Germany) at magnifications of 10 and 40 to observe the characteristics of the particles, transparency, size and dispersion of the extracted silica.

6. Study of the functional groups of extracted silica

The prepared rice husk samples and the extracted silica were analyzed for functional groups using a Fourier Transform Infrared (FT-IR) spectrometer, model IRTracer-100, SHIMADZU, Japan. The samples were prepared using the Attenuated Total Reflection (ATR) technique on a diamond crystal and the measurements were recorded in the wavenumber range of 400-4000 cm^{-1}.

7. Brunauer–Emmett–Teller (BET) Analysis of Silica

The specific surface area of the silica produced from rice husk was evaluated using the nitrogen BET adsorption technique.

8. Efficiency Testing of Methylene Blue Absorption

8.1 Study of absorption efficiency

The experimental procedure to test the absorption properties of the extracted silica was as follows:

- Prepare a methylene blue solution at a concentration of 500 mg/L, with dilutions ranging from 20 to 200 mg/L.
- Prepare methylene blue solutions at concentrations of 0, 20, 40, 60, 80 and 100 ppm.
- Plot the absorbance values obtained to create a standard graph depicting the relationship between absorbance and concentration.
- Weighed each type of raw material, extracted silica and commercial-grade silica, 0.10 g each and pour into 250 mL conical flasks. Then fresh methylene blue solution was added with concentrations of 20, 40, 60, 80, 100, 125, 150 and 200 mg/L, each with a volume of 50 mL. The mixtures were shaken at room temperature for 24 hr. Afterwards, the solutions were filtered and analysed using a UV-VIS, model 1280 manufactured, SHIMADZU, Japan measuring at a wavelength of 600 nm. The calculation of the total amount of methylene blue adsorbed by silica (mg/g) usedthe equation below (Liu et al., 2018).

$$Q_e = \frac{V(C_0 - C_e)}{W}$$

Where: Q_e is the ability to adsorb the adsorbate at the equilibrium point of silica (mg/g).
C_o is the initial concentration of MB (mg MB/l) in the liquid phase before the reaction.
C_e is the concentration of MB (mg MB/l) in the liquid phase at equilibrium.
V is the volume of the methylene blue solution (l).
W is the mass of dried silica (g).

8.2 Study of isotherm adsorption by Langmuir and Freundlich models

Studying the isotherm adsorption of Langmuir and Freundlich by using the values of methylene blue adsorption, the values of C_e and Q_e were calculated. Subsequently, the values of 1/ C_e and 1/Q_e were plotted to find the relationship between 1/ C_e and 1/Q_e on the Langmuir equation, as shown in the equation below.

$$\frac{1}{Q_e} = \frac{1}{Q_m K_L}\frac{1}{C_e} + \frac{1}{Q_m}$$

Where: Q_m is Maximum monolayer adsorption capacity (mg MB/g).
K_L is Langmuir Isotherm constant.

In the study of isotherm adsorption using the Freundlich model, C_e and Q_e values were utilized to calculate log C_e and log Q_e . Subsequently, a graph was plotted to establish the relationship between log C_e and log Q_e based on the Freundlich equation, as expressed in the equation below.

$$\log Q_e = \frac{1}{n}\log C_e + \log K_F$$

where: K_F is constant indicating the adsorption capacity of the multilayer adsorption (mg/g)
n is Constant of the Freundlich Isotherm describing the intensity of adsorption.

For the experiments conducted in this research, each experiment was repeated three times and the reported results are presented as averages (Pramual 2014).

Results and discussion

1. Percent yield of prepared sample

The raw rice husk and black rice husk ash, after the burning process, yielded 0.53 g and 4.25 g, respectively. This was obtained from an initial raw material weight of 5 g, resulting in percent yields of 10.68% and 85.04%, respectively, as shown in Table 1. The burning process serves to eliminate impurities or other organic substances, leading to a higher silica content. The experiment indicates that the raw rice husk after burning has a lower yield percentage compared to black rice husk ash, suggesting that raw rice husk contains more impurities than black rice husk ash.

Table 1 Percent yield of prepared sample

Raw materials	Initial weight (g)	Weight after burning (g)	Percent Yield (%)
Raw rice husk	5.00	0.53	10.68
Black rice husk ash	5.00	4.25	85.04

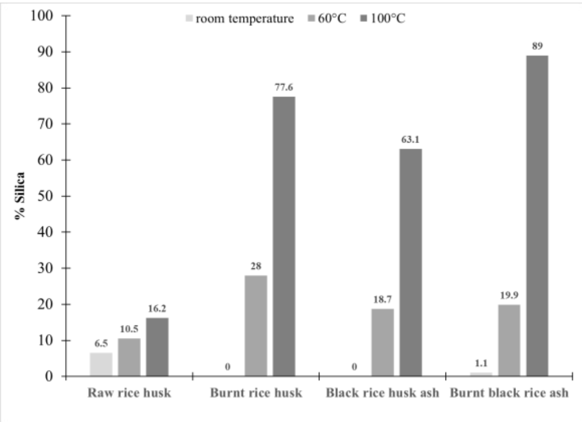
2. Optimal conditions for silica extraction and precipitation

The percent yield of extracted silica from raw rice husk and black rice husk ash using materials that underwent acid leaching and those that did not undergo acid leaching is presented in Fig. 2a and 2b, respectively. The influence of temperatures on silica extraction is illustrated.

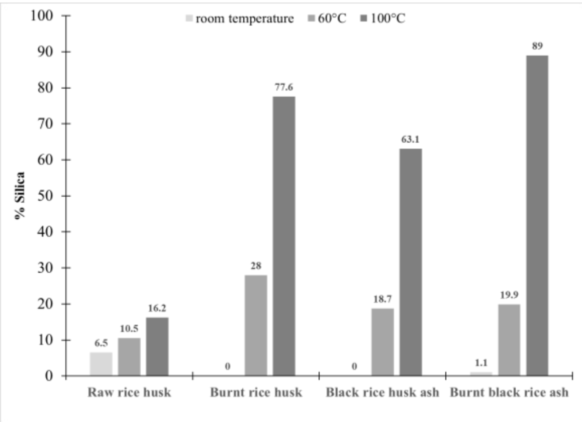
From Fig. 2a, it is observed that as the extraction temperature for silica increases, the amount of extracted silica also increases. The temperature of 100°C was found to be the most suitable for extraction, yielding the highest percentage of extracted silica. The highest percentages of extracted silica at 100°C were 16.2%, 77.6%, 63.1% and 89.0% for raw rice husk, burnt rice husk, black rice husk ash and burnt black rice husk ash, respectively. The process of extracting silica using HCl acid at different temperatures, or through pyrolysis processes involving acid, involves the decomposition of organic substances and various contaminants. As the temperature increases, the decomposition of organic substances occurs more effectively compared to lower temperatures.

However, when using raw materials that did not underwent acid leaching, it was found that burnt rice husk, black rice husk ash and burnt black rice husk ash yield the highest percentage of silica when the extraction temperature was 100°C. The percentage of extracted silica from not undergoing acid pretreatment of raw rice husk at a temperature of 60°C and 100°C had close values because raw rice husk which had not underwent acid pretreatment had a large amount of contamination and even raising the temperature of extraction might not change the percentages of extracted silica value. These temperatures provide similar percentages of extracted silica, as shown in the comparison of extracted silica percentages from raw materials that did not undergo acid leaching in Fig. 2b.

When studying the efficiency of separating sodium silicate in the form of a solution, the solution was adjusted to a neutral pH using hydrochloric acid with a concentration of 1 M. This process results in the precipitation of silica. The weight of the obtained silica is then measured and the percentage of silica precipitation is calculated. The results are presented in Table 2.



(a) Samples underwent acid leaching



(b) Samples did not undergo acid leaching

Fig. 2 Percentage of extracted silica at various extraction temperatures

Table 2 Percentage of efficiency of sodium silicate separation and the percentage of silica precipitation

Sample	Sodium silicate separation (%)		Silica precipitation (%)	
	Leached with HCl	Not leached with HCl	Extracted with HCl	Not leached with HCl
Raw rice husk	39.1	58.7	16.2	9.1
Burnt rice husk	71.5	64.5	77.6	66.6
Black rice husk ash	59.2	60.3	63.1	58.1
Burnt black rice husk ash	63.7	62.0	89.0	72.2

In comparing the efficiency of separating sodium silicate and the precipitation of silica, it was found that burnt raw rice husk and burnt black rice husk ash yield a higher percentage of sodium silicate separation than raw rice husk and black rice husk ash. When comparing the raw materials that underwent acid leaching and those that did not, it was observed that the raw materials subjected to acid leaching were more effective in separating sodium silicate. When taking the sodium silicate solution and adjusting its conditions to be neutral with HCl at a concentration of 1 M, silica precipitation occurred. When calculating the percentage of silica precipitation obtained, it was found that the percentages followed a similar trend to the percentage of sodium silicate separation. This is because sodium silicate can dissolve in water. A higher percentage of sodium silicate separation indicates a greater amount of dissolved sodium silicate in the solution. When adjusting the pH with HCl, the concentration of 1 M makes it more difficult for sodium silicate to dissolve, leading to silica precipitation. This results in a higher percentage of silica precipitation.

From the comparison of the amount of silica obtained from raw materials that underwent acid leaching and silica from raw materials that did not undergo acid leaching, it was found that silica obtained from materials subjected to acid leaching yielded a higher quantity. Therefore, it indicates that the temperature used in the burning process helps eliminate impurities or various organic substances, resulting in higher quantities of silica.

3. Results of the physical properties of extracted silica

When various raw materials and extracted silica were ground finely using a mortar and screened through sieves of No.100 (150 μm), No.120 (125 μm) and No.270 (53 μm), it was found that all types of raw materials could pass through the 150 μm sieve but not through the 125 μm sieve. This indicates that the particle size of the raw materials falls within the range of 125-150 μm. Extracted silica from various raw materials, both those that underwent acid leaching and those that did not, could pass through the 53 μm sieve, indicating that the obtained silica has a size smaller than 53 μm.

When various raw materials and extracted silica were examined using an inverted microscope at magnifications of 10 and 40 times to study the physical characteristics, such as particle morphology, size, color and transparency of the raw materials and extracted silica from different raw materials, both those that underwent acid leaching and those that did not. When compared, the micrographs in Fig. 3 will illustrate the characteristics of the particles.

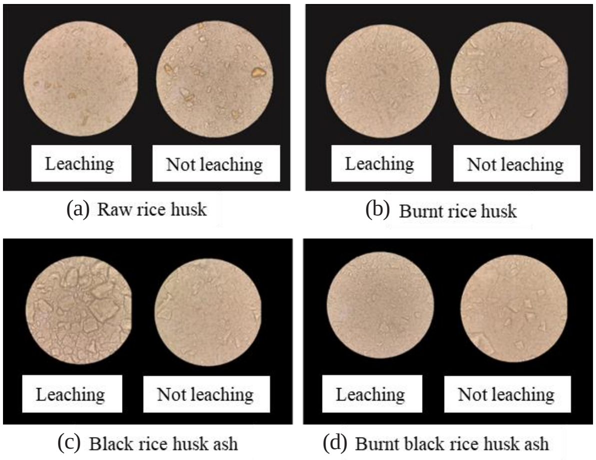


Fig. 3 Characteristics of the silica particles extracted

Upon studying the characteristics of the extracted silica by comparing between the silica extracted from raw materials that underwent acid leaching and those that did not, it was found that the extracted silica from raw materials includes:

- Silica extracted from raw rice husk, when subjected to acid leaching, will exhibit characteristics of clear and slightly yellowish silica particles with a uniform size. In contrast, silica that did not undergo acid leaching will have noticeably different sizes as shown in Fig. 3a.
- Silica obtained from burnt raw rice husk, when subjected to acid leaching, will have clearer characteristics without any color tint and the particles will have a uniform size. Similarly, silica that did not undergo acid leaching will exhibit different particle sizes as shown in Fig. 3b.
- Silica extracted from black rice husk ash, when subjected to acid leaching, will have characteristics of clear particles with a grayish tint and the particles will have a uniform size as shown in Fig. 3c.

- Silica from burnt black rice husk ash, when subjected to acid leaching, will have clearer characteristics and the particles will be uniform in size, with no added color as shown in Fig. 3d.

The particle sizes of the silica that underwent acid leaching were close to each other, while the sizes of silica that did not undergo acid leaching differed noticeably. Therefore, it is evident that subjecting raw materials to high-temperature burning before extraction, followed by acid leaching, results in cleaner silica with more uniform particle sizes.

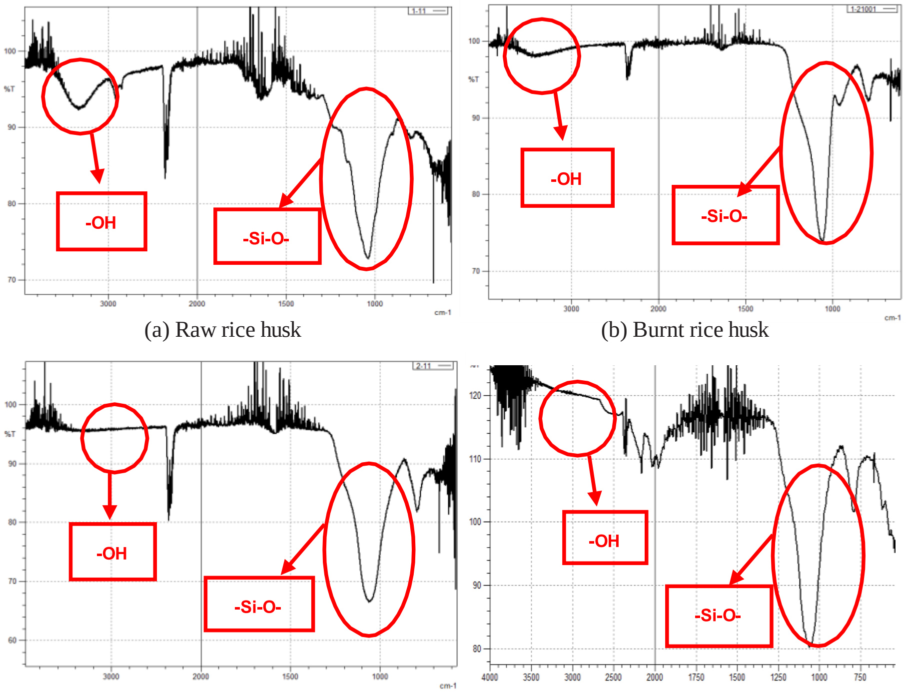
4. Functional group analysis using FT-IR Technique

The results of the functional group analysis using the FT-IR technique for various raw materials are presented in Figs. 4-6.

From Fig. 4, when analyzing different raw materials, including raw rice husk, burnt raw rice husk, raw black rice husk ash and burnt black rice husk, for functional groups, it is observed that all types of raw materials provide signals at the same wavenumber. Notably, signals appear at the wavenumber of 3400 cm^{-1}, corresponding to the hydroxyl (-OH) functional group, indicating stretching vibrations. In addition, the IR spectra at wavenumbers 1090 and 801 cm^{-1} represent the functional group of siloxane (-Si-O-Si-), demonstrating stretching vibrations. These signals are crucial for confirming the presence of silica functional groups. This illustrates that various raw materials contain silica as a common component.

From Fig. 5, when the extracted silica from various raw materials leached with acid is analyzed for functional groups, it is observed that silica obtained from all types of raw materials provides signals at the same wavenumbers as the original raw materials. The signals are particularly noticeable at wavenumbers 3400 cm^{-1} and 1090, 801 cm^{-1}. The extracted silica appears to be cleaner, as indicated by the clearer and more distinct signals on the IR spectrum compared to the original raw materials. This is evident when comparing the characteristics of the signals on the spectra between Figs. 4 and 5.

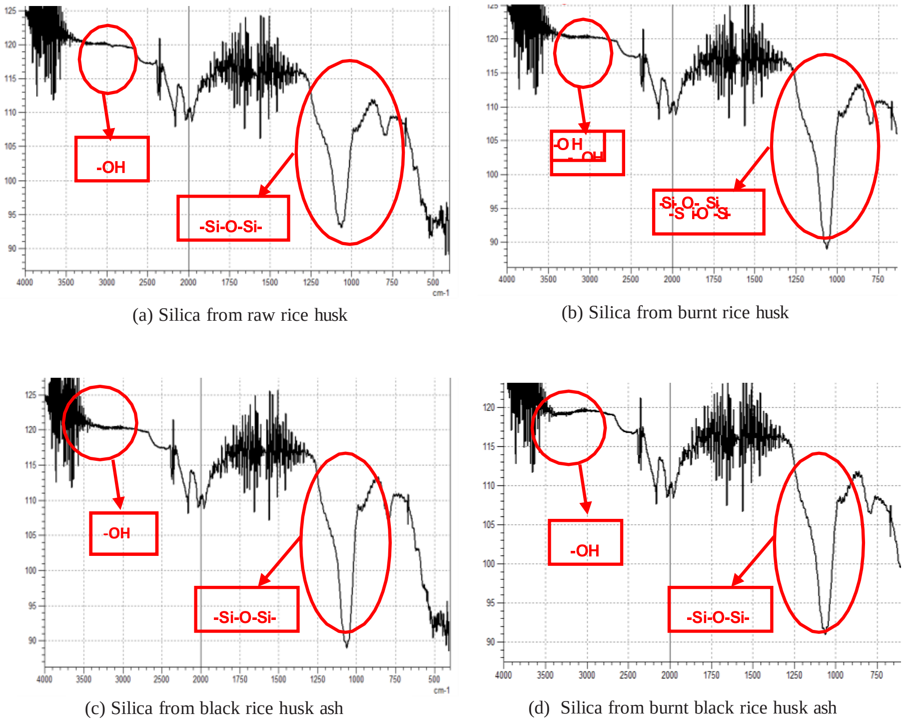
In Fig. 6, when the extracted silica from various raw materials that were not leached with acid and was analyzed for functional groups, it was observed that silica obtained from all types of raw materials provides signals at the same wavenumbers as the silica extracted from raw materials leached with acid. Therefore, it can be concluded that the analysis of functional groups



(a) Raw rice husk (b) Burnt rice husk

(c) Black rice husk ash (d) Burnt black rice husk ash

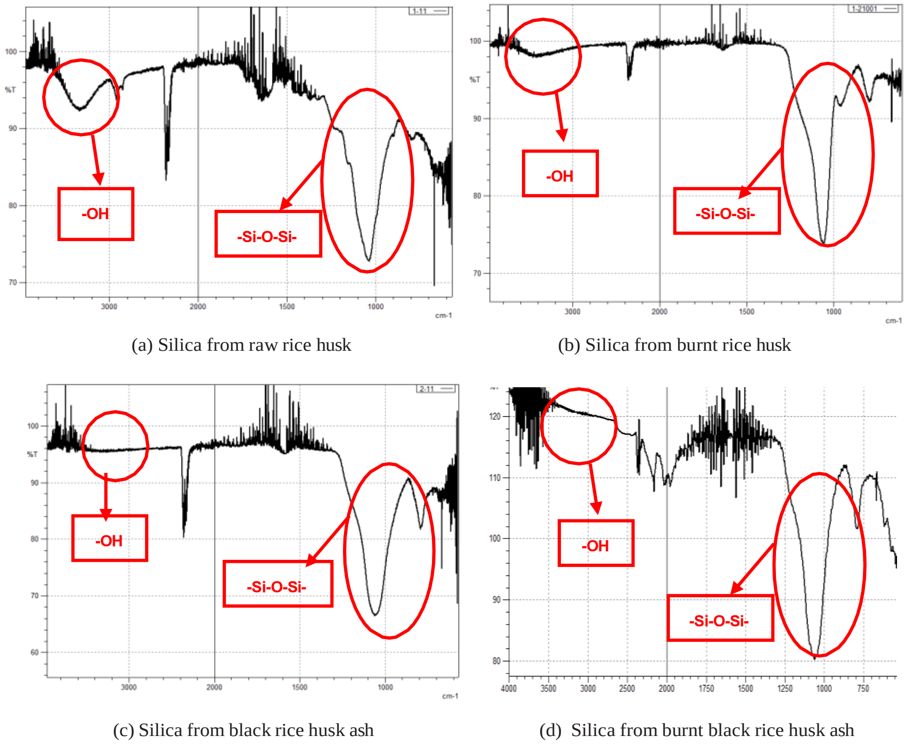
Fig. 4 IR spectrum of various raw material



(a) Silica from raw rice husk (b) Silica from burnt rice husk

(c) Silica from black rice husk ash (d) Silica from burnt black rice husk ash

Fig. 5 IR spectrum of extracted silica from raw materials leached with acid



(a) Silica from raw rice husk (b) Silica from burnt rice husk

(c) Silica from black rice husk ash (d) Silica from burnt black rice husk ash

Fig. 6 IR spectrum of extracted silica from raw materials not leached with acid reveals that silica is present in all types of raw materials. The extracted silica from raw materials that have undergone acid treatment and those that have not undergone acid treatment both exhibit signals at the same wavenumbers. Consequently, it can be inferred that the silica obtained from raw materials that have undergone acid treat

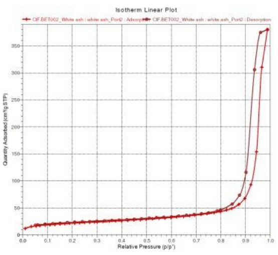
5. Results of Brunauer–Emmett–Teller (BET) Analysis of Silica

The surface area, pore volume, pore diameter and particle size of silica synthesized from rice husk were analyzed using BET. Table 3 presents a summary of the results for total pore volume, specific surface area and average diameter of silica. The study found that silica extracted from burnt rice husk had a particle size of 80.3 nm, smaller than that of silica obtained from burnt black rice husk ash, which had a particle size of 125.4 nm. Consequently, silica derived from burnt rice husk exhibited greater surface area, pore volume and pore diameter. Specifically, silica from burnt rice husk had surface area and pore volume values of 74.75 m^2/g and 0.30 cm^3/g, respectively. When comparing silica extracted from burnt rice husk without acid treatment to that treated with HCl, it was observed that acid-treated silica had a reduced particle size from 80.3 nm to 50.5 nm and increased surface area, pore volume and pore diameter, with values of 118.73 m^2/g and 0.57 cm^3/g, respectively (Dhaneswara et al., 2020).

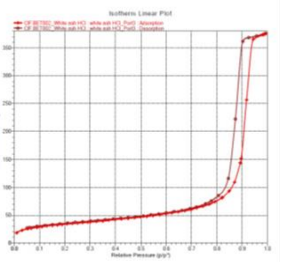
Table 3 BET surface area of silica produced

Sample	BET surface area, m^2/g	Total pore volume, cm^3/g	Average pore diameter, nm	Average particle size, nm
Silica from burnt rice husk not leached with HCl	74.75	0.30	15.76	80.3
Silica from burnt rice husk leached with HCl	118.73	0.57	19.15	50.5
Silica from burnt black rice husk ash not leached with HCl	47.83	0.10	8.14	125.4
Silica from burnt black rice husk ash leached with HCl	69.44	0.24	13.99	86.4
Commercial-grade Silica (Particle Size < 63 µm)	182.28	0.71	15.61	32.9

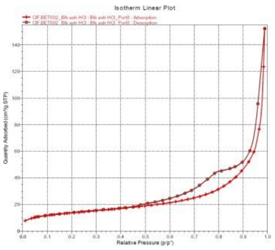
As Table 3 shows, the pore diameter of the silica obtained from the extraction process is about 8.14–19.15 nm. This indicates that the silica is a mesoporous material. A mesoporous material is a material whose pores measure less than 50 nm in diameter. Thus, it can be concluded that silica extracted from rice husk using an alkaline extraction process produces silica mesoporous nature. The adsorption behaviors of silica produced from rice husk are shown in Fig.7. In Fig. 7, the upper portion of a loop is recognized as desorption and the lower portion is adsorption. The adsorption behaviors possess a type IV isotherm. The type IV isotherm indicates a mesoporous material and the shape of the pore is cylinder (Ambroz et al., 2018).



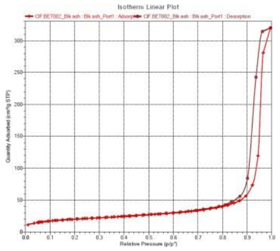
(a) Silica from burnt rice husk not leached with HCl



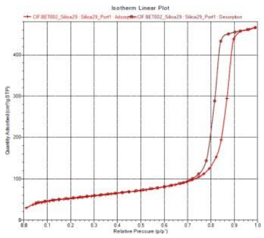
(b) Silica from burnt rice husk leached with HCl



(c) Silica from burnt black rice husk ash not leached with HCl



(d) Silica from burnt black rice husk ash leached with HCl



(e) Commercial-grade Silica

Fig. 7 Adsorption-desorption isotherms of nitrogen for samples extracted

6. Results of methylene blue adsorption efficiency test

In the experiment, solutions of methylene blue were prepared with concentrations of 0, 10, 20, 30, 40 and 50 ppm. When the concentration of the methylene blue solution and the absorbance values were plotted, a linear relationship was obtained. The regression equation for the graph is given by y = 0.0196x - 0.0267, with an R^2 value of 0.9970. The R^2 value approaching 1 indicates a highly reliable correlation, suggesting that the graph follows a linear trend.

A quantity of 0.05 g of commercial-grade silica and silica extracted from the acid-leached material at a temperature of 100°C was weighed. These samples, along with the raw materials subjected and not subjected to the acid leaching, were used for adsorbing a methylene blue solution with a concentration of 100 ppm in a volume of 50 mm. The mixtures were agitated at room temperature for 24 hr to observe the equilibrium of the adsorption.

Subsequently, the adsorbed solution was measured for absorbance at a wavelength of 600 nm. The absorbance values were then compared with a standard graph to calculate the remaining quantity of methylene blue at equilibrium (C_e). The percentage adsorption was determined. The results are summarized in Table 4.

Table. 4 Adsorption efficiency of methylene blue by extracted silica compared with commercial-grade silica

Raw materials	Adsorbed Methylene Blue quantity (mg MB/g)		Adsorption (%)	
	Leached with HCl	Not leached with HCl	Leached with HCl	Not leached with HCl
Silica from raw rice husk	1457.56	1302.49	73.61	65.78
Silica from burnt rice husk	1371.18	1706.35	69.24	86.17
Silica from black rice husk ash	1653.56	1648.00	83.51	83.22
Silica from burnt black rice husk ash	1671.56	1565.23	83.58	78.89
Commercial-grade Silica (Particle Size < 63 µm)	230		23.76	

The results of the study on the adsorption efficiency of methylene blue by silica extracted from raw materials, subjected and not subjected to acid leaching processes, were compared to commercial grade silica. The results revealed that the extracted silica from materials subjected to acid leaching can adsorb a quantity of methylene blue in the range of 1371.18-1671.56 mg MB/g, with an adsorption efficiency ranging from 69.24% to 83.58%. On the other hand, the extracted silica from materials not subjected to acid leaching showed adsorption efficiency ranging from 1302.49-1706.35 mg/g, with an adsorption efficiency of 65.68-86.17%. When comparing the adsorption efficiency of both types, it is evident that the acid-leached silica has comparable adsorption efficiency, while the commercial grade silica has a lower adsorption efficiency at 230 mg MB/g, equivalent to 23.76%.

7. Results of the study of adsorption isotherms using Langmuir and Freundlich models

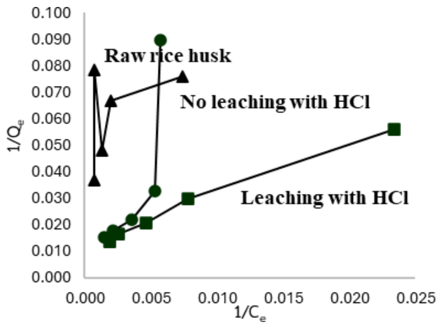
The results of the study of adsorption isotherms using Langmuir and Freundlich models by taking Q_e values for raw rice husk, burnt rice husk, black rice husk ash and burnt black rice husk ash at the extraction temperature of 100°C are presented in Figs. 8-12.

In Figs 8a and 8b, a comparison of Langmuir adsorption isotherms for raw materials, both with and without acid leaching, is presented. It is observed that the silica extracted from raw materials subjected to acid leaching exhibits a more linear trend in the graph compared to the starting raw materials. This suggests that the silica obtained from raw materials subjected to acid treatment has enhanced adsorption characteristics. The analysis considers the slope values and R^2 values to understand the trend and reliability of the adsorption.

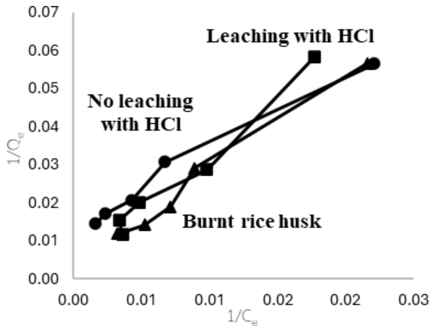
Upon comparing the adsorption characteristics graph for the Langmuir isotherm of burned black rice husk ash, burnt black rice husk and silica obtained from two types of raw materials, it is observed that the graph exhibits a more linear trend compared to the starting raw materials. This is consistent with the observations from Fig. 8c and 8d. Therefore, silica extracted from raw materials subjected to acid leaching is further studied for its adsorption characteristics using the Langmuir adsorption isotherm.

Upon comparing the Freundlich adsorption isotherm graph of raw rice husk, burnt rice husk and silica obtained from two types of raw materials, both subjected and not subjected to acid leaching, the results are shown in Fig. 9. It can be observed from the graph lines that silica extracted from raw materials subjected to acid leaching exhibits a more linear trend compared to the starting raw materials and silica extracted from raw materials not subjected to acid leaching.

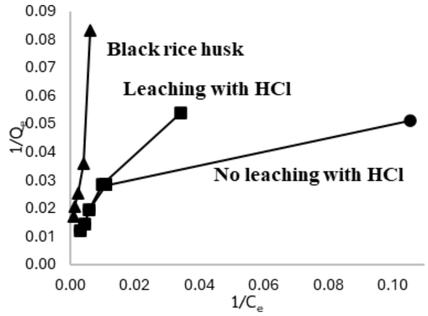
When comparing the adsorption graph characteristics of the Freundlich isotherm of black rice husk, burnt black rice husk and silica obtained from two types of raw materials, both subjected and not subjected to acid leaching, it is observed that the graph lines exhibit a more linear trend compared to the starting raw materials. Therefore, silica extracted from raw materials that have undergone acid was studied to observe the Freundlich adsorption isotherm, Langmuir adsorption isotherm, examining the slope and R^2 values as shown in Figs. 10 and 11.



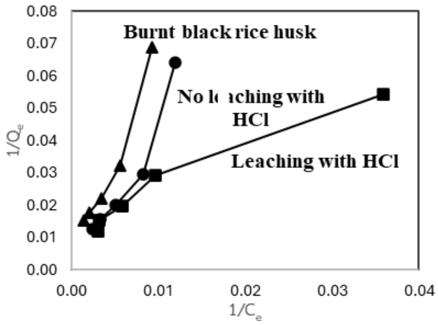
a) Raw rice husk and extracted silica



b) Burnt rice husk and extracted silica

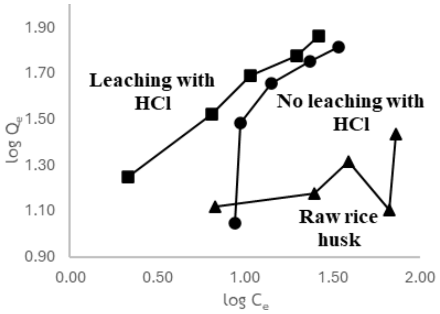


c) Black rice husk ash and extracted silica

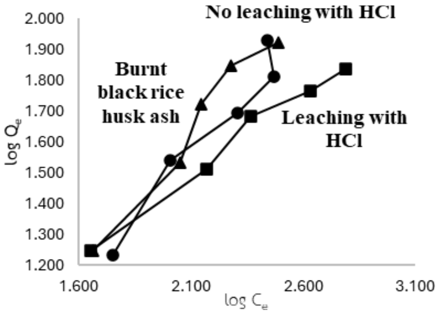


d) Burnt black rice husk ash and extracted silica

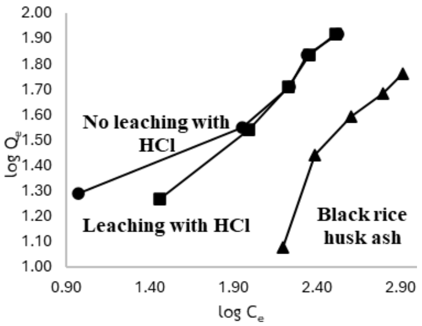
Fig. 8 Langmuir adsorption isotherm of raw materials and extracted silica



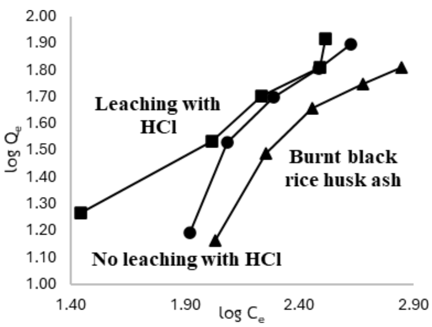
a) Raw rice husk and extracted silica



b) Burnt rice husk and extracted silica

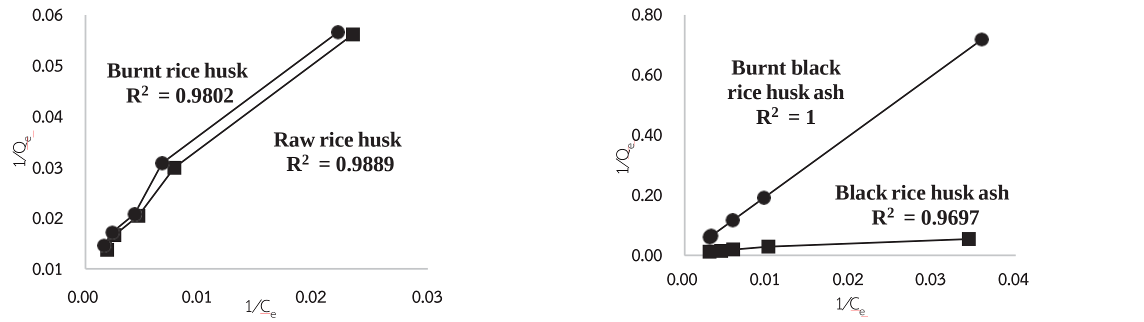


c) Black rice husk ash and extracted silica



d) Burnt black rice husk ash and extracted silica

Fig. 9 Freundlich adsorption isotherm of raw materials and extracted silica



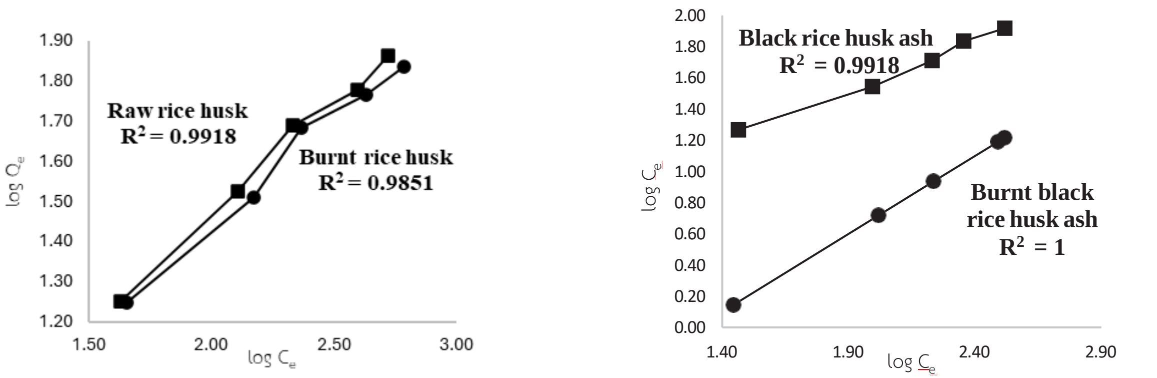
(a) Silica extracted from raw rice husk and burnt rice husk (b) Silica extracted from black rice husk ash and burnt black rice husk ash

Fig. 10 Langmuir adsorption isotherm of silica extracted from raw materials leached with HCl at 100°C

From the characteristics of the graph, when calculating the slope and R^2 values on the Langmuir equation, Fig. 10 reveals that the adsorption characteristics of silica extracted from raw materials subjected to acid leaching have R^2 values of 0.9889, 0.9802, 0.9697 and 1 for silica obtained from raw materials of raw rice husk, burnt rice husk, black rice husk ash and burnt black rice husk ash, respectively.

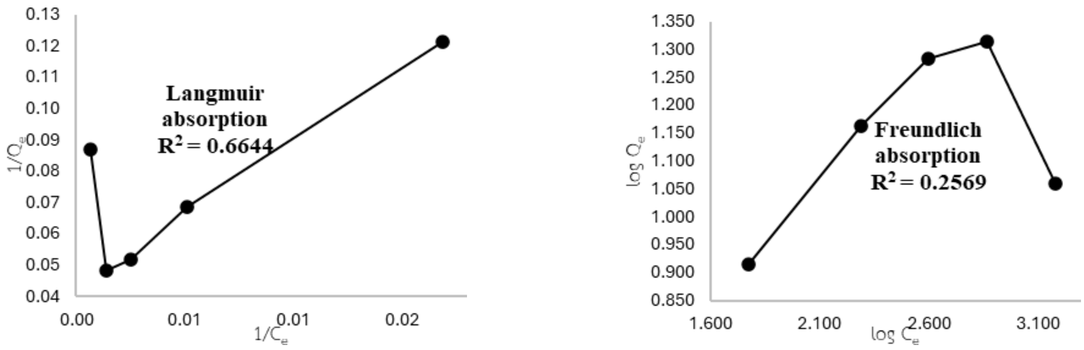
When comparing the graph of silica obtained from raw materials subjected to acid leaching to observe the trend of Freundlich adsorption isotherm, the results are shown in Fig. 11. The R^2 values for raw rice husk, burnt rice husk, black rice husk ash and burnt black rice husk ash are 0.9918, 0.9851, 0.9918 and 1, respectively. Considering the R^2 values close to 1, it is found that burnt rice husk, burnt rice husk and black rice husk ash exhibit an adsorption isotherm consistent with the Freundlich equation, indicating a multi-layer adsorption. However, burnt black rice husk ash shows characteristics aligned with both the Langmuir and Freundlich equations, indicating a mono-layer and multi-layer adsorption.

When studying the adsorption isotherm of commercial-grade silica using both Langmuir and Freundlich models, the characteristics of the graph are presented in Fig.12a and Fig.12b respectively. From the graph, it is observed that the R^2 values for commercial-grade silica are 0.6644 and 0.2569 for Langmuir and Freundlich isotherms, respectively. Therefore, it can be seen that the adsorption characteristics of commercial-grade silica align with the Langmuir equation, exhibiting a mono-layer adsorption pattern.



(a) Silica extracted from raw rice husk and burnt rice husk (b) Silica extracted from black rice husk ash and burnt black rice husk ash

Fig. 11 Freundlich adsorption isotherm of silica extracted from raw materials leached with HCl at 100°C



(a) Langmuir adsorption isotherm (b) Freundlich adsorption isotherm

Fig. 12 Adsorption isotherm of commercial-grade silica

From the study of the adsorption isotherm, it was found that silica extracted from various raw materials exhibits a multi-layer adsorption pattern. This multi-layer adsorption characteristic contributes to a higher efficiency in adsorbing methylene blue compared to commercial-grade silica. This is because commercial-grade silica tends to have a mono-layer adsorption pattern. From the BET analysis, it was found that commercial silica has a particle size of 32.9 nm and a surface area of 182.28 m2/g. These particles are smaller than the extracted silica particles, but they have a larger surface area, resulting in the adsorption of methylene blue occurring in a mono-layer adsorption.

Conclusion

From the study of extracting and precipitating silica from rice husk using the hydrothermal method in a base medium from various types of raw materials, including raw rice husk, burnt rice husk, black rice husk ash and burnt black rice husk ash, samples were prepared for sodium silicate precipitation. The samples were divided into two sets: those that underwent acid leaching and those that did not. When extracting and precipitating sodium silicate at different temperatures, it was found that the suitable temperature for sodium silicate precipitation was 100°C.

Silica extracted from raw materials that underwent acid leaching yielded higher quantities compared to silica from raw materials that did not undergo acid leaching. The silica content in raw rice husk, burned rice husk, black rice husk ash and burned black rice husk ash was 16.20%, 77.60%, 63.10% and 89.0%, respectively. The physical characteristics study revealed that silica obtained from acid-leached raw materials had uniform particle sizes, all less than 53 µm.

From the Brunauer–Emmett–Teller (BET) analysis of silica, it was observed that the extracted silica possesses a pore diameter ranging from 8.14 to 19.15 nm, indicating its mesoporous nature. Silica obtained from burnt rice husk that underwent acid leaching with HCl has smaller particle sizes compared to silica obtained from untreated burnt rice husk. Specifically, silica derived from burnt rice husk leached with HCl exhibits particle sizes and surface areas closest to commercial-grade silica.

Examining all the extracted silica using FT-IR spectroscopy, signals of the siloxane group (-Si-O-Si-) at wavenumbers 1,090 and 801 cm^{-1} and the hydroxyl group (-OH) at wavenumber 3,400 cm^{-1} were observed. Evaluating the adsorption efficiency for methylene blue, it was found that the extracted silica had a better adsorption capacity than commercial-grade silica. The adsorption values ranged from 1302.49 to 1706.35 mg MB/g, equivalent to 65.78-86.17%.

From the adsorption isotherm study for methylene blue with the extracted silica from all types of raw materials, it was observed that the adsorption behaviour followed the Freundlich equation, indicating multi-layer adsorption. The hydrothermal method for silica extraction and precipitation in a base medium proves to be an effective method for preparing micro-level silica.

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