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Synthesis and Characterization of Zeolite Sourced from Rice Husk Lignocellulosic Waste Ash

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ABSTRACT
Rice husk, typically deemed a byproduct in the rice industry, presents a promising avenue for the production of valuable materials including zeolites, which are highly sought-after as crucial adsorbent support materials. This study intricately focuses on the synthesis of zeolites utilizing rice husk ash (RHA) as the SiO_2 source with a Fourier-Transform Infrared (FTIR) analysis guided optimized addition of aluminum from external sources. The produced zeolite, as evidenced by the FTIR spectrum, showcases distinct functional groups associated with zeolite formation, notably the -O-H band at 2851 cm^{-1} and the bending vibration of adsorbed water molecules at 1659 cm^{-1}. Prominent Si-O-Si, Al-O, and Si-O-Al functional groups absorbed further validate zeolite framework formation. Employing a straightforward method involving alkaline extraction and acid precipitation, the study successfully yields pure silica xerogel from this waste, minimizing mineral contaminants. The resulting xerogel demonstrates 91% silica content and 2.6-4% moisture. Subsequent water washing proves effective in further reducing mineral content (Na < 200ppm, K < 400ppm). X-ray Diffraction (XRD) analysis of the zeolites reveals the amorphous nature of silica xerogels, emphasizing their heightened activity for zeolite Y and P production. This comprehensive investigation not only underscores the potential for converting rice husk waste into valuable materials but also contributes to sustainable and efficient utilization practices.

Keywords: Rice Husk, Silica, Zeolites

INTRODUCTION
The production and use of renewable biomass has emerged as one of the global trends in recent years. The leftovers of plants and animals that are converted into heat or electricity are called biomass (Antar *et al.*, 2021). Additionally, it serves as a raw material for a variety of products in a variety of industrial processes (Ghani *et al.*, 2015). Plants provide cheap, plentiful, lignocellulose-rich materials known as "plant biomass" that can be used for renewable purposes (Chen, 2015). A vast amount of trash is produced during the agricultural production of many crops, including mustard, chile, cotton, sugarcane, sweet sorghum, pulses, oilseeds, sorghum, etc. in many countries, including Nigeria. These wastes are either burned or abandoned in the fields without finding another use. As a result, these could be effective substitute resources for producing a variety of beneficial goods in an eco-friendly way (Kim & Dale, 2004). The majority of lignocellulosic biomass produced in the agriculture sector is produced by maize, wheat, rice, and sugarcane; the remaining crops account for a very small part of global production (Laureano-Perez *et al.*, 2005). Studies have shown that lignin (15–25 percent w/w), hemicellulose (23–32 percent), and cellulose (38–50 percent) are the main constituents of a typical lignocellulosic biomass (Mamman *et al.*, 2008).

The crystalline nanoporous minerals known as zeolites are widely used in several fields, particularly for their usefulness as adsorbents, catalysts, and detergent formulation ingredients (Eroglu, Emekci, & Athanassiou, 2017). Zeolites have several characteristics that make them ideal for catalyzing reactions involving organic compounds. These characteristics include their crystalline structure, resistance to deactivation by carbon deposition, uniform microporosity, high surface area, hydrophobicity, and shape selectivity (Rinaldi & Schüth, 2009). Zeolites are being used on a commercial basis in several important sectors for these and other reasons. In the cases of fine chemistry, pollution abatement, and the oil and petrochemical sectors, zeolites have been used to enable the development of numerous commercial applications (Perego & Bosetti, 2011). The use of zeolites as catalysts in biomass valorization processes to make biofuels and/or bio-based chemicals that could lead to the substitution of fossil fuels with renewable ones is another developing subject that has attracted a lot of attention recently. The role of renewable energy sources in the production of heat and power is growing (Conti *et al.*, 2016)

Although silica is the most common oxide in the earth's crust, it is mostly produced artificially for use in technology. Nevertheless, silica is an important inorganic multifunctional chemical molecule (Londeree, 2002). An alternate supply of naturally occurring silica can be used in place of commercial silica precursors, particularly those found in agricultural waste (Mane & Babu, 2011). Among the extensively researched agricultural wastes that have been transformed into more valuable final products are rice husk sawdust and rapeseed stalk (Novie *et al.,* 2016).

All zeolites are based on an aluminosilicate framework, which is composed of four oxygen anions surrounding a tetrahedral arrangement of silicon (Si^{4+}) and aluminum (Al^{3+}) cations (O^{2-}). The SiO_2 and AlO_2 tetrahedral building blocks, which are shared by two tetrahedrons and each oxygen ion in the Si-O and Al-O linkages joining two cations, form a macromolecular three-dimensional framework. With this atom arrangement, a Si or Al cation is surrounded by four O atoms in each tetrahedron, resulting in a three-dimensional structure of silicate tetrahedra with a 1:2 Si:O ratio(Armbruster & Gunter, 2001). When some Si^{4+} ions are swapped out for Al^{3+} ions, the tectosilicate structure gains a net negative charge. The formal valency difference between the $(AlO_4)_{5-}$ and $(SiO_4)_4$ is what generates this charge.

This research aim to synthesize and characterize zeolite from rice husk, focusing on its potential applications in various fields. The objectives include collecting rice husk samples to determine the presence of silica as precursor for zeolite synthesis, followed by the synthesis and characterization of zeolite using laboratory-sustainable methods. The study seeks to demonstrate the practical utility of agricultural waste, such as rice husk, by synthesizing zeolite content for environmental, industrial, and laboratory purposes. The significance of this research lies in showcasing the diverse applications and untapped potentials of agricultural waste, with zeolite serving as a versatile material for applications like catalyst support, adsorption, drying agents, and the separation and purification of gases and liquids. This exploration contributes to a better understanding of the valuable constituents within agricultural waste, emphasizing their role in synthesizing both organic and inorganic compounds through various methods.

MATERIALS AND METHODS:

Various reagents were employed to synthesize zeolite from rice husk. Sodium hydroxide (NaOH) 97%, sulfuric acid (H_2SO_4) 95%, rice husk, and distilled water constituted the fundamental components of the experimental setup. Ammonium hydroxide (NH_4OH) 33%, hydrochloric acid (HCl) solution 38%, potassium chromate (K_2CrO_4) 99%, and aluminum sulfate ($Al_2(SO_4)_3.H_2O$ 99% were utilized to facilitate specific stages of the synthesis process. Additionally, sodium hydroxide pellets 97%, tetrapropylammonium bromide ($(CH_3CH_2CH_2)_4N(Br)$ 98%, and silver nitrate ($AgNO_3$) 99% played integral roles in achieving the desired outcomes. Sodium carbonate (Na_2CO_3) 99% and ethanol (CH_3CH_2OH) 95% were employed for washing and purification steps throughout the experimental stages, ensuring the quality and integrity of the synthesized zeolite. All the chemicals were supplied by Sigma Aldrich and Fischer scientific.

Experimental Design

The research work unfolded in three distinct stages, each serving a specific purpose.

Stage 1: Preparation of Ash from Rice Straw

The preliminary stage involved the examination of lignocellulosic wastes, encompassing physical scrutiny, sample collection, and subsequent incineration to ash. Diverse lignocellulosic wastes underwent treatment to convert silica, guided by established methodologies (Rupasinghe *et al*., 2023).

Stage 2: Extraction of Silica from Prepared Rice husk Ash

After gently heating 10g of ash with 3M NaOH in a 1:7 ratio for 30 minutes at 80–90°C, the mixture was allowed to cool at ambient temperature and was filtered to eliminate carbon impurities that had not burned. The resultant solution was concentrated for 90 minutes at 100–150°C to produce a gelatinous sodium silicate and was measured using a weighing balance. After adding 12N concentrated sulfuric acid to the solution to bring it down to pH 3–4, silica is then precipitated, and sodium sulfate remains as a byproduct. 50ml distilled water was added to the solution cooled for half an hour, and it was left to age for a whole night to regulate the exothermic process. After centrifuging the silica gel to remove the supernatant, the gel was dried for six hours at 80°Cto produce the silica and the percentage yield was then determined (Rungrodnimitchai *et al.*, 2009).

Stage 3: Synthesis of Zeolite

6.6gm NaOH was dissolved in 55ml distilled water, 8gm SiO_2 was dissolved, and the solution was stirred until a clear solution was obtained (solution A). Another 6.6gm NaOH dissolved in 55ml distilled water and 3.3gm of $Al_2(OH)_3$ was added and the solution was stirred until a clear solution was obtained (solution B). Solution A and solution B were added together, and pH was adjusted to 11 and the solution was stirred for 1 hour at room temperature using a magnetic stirrer. The solution was kept at 90^{o}c for 4 days. The solid material/powder obtained was washed again using distilled water to reduce the pH to 8 and finally the sample is dried in oven for 6hours at 100°C and zeolite is obtained (Bajpai *et al*., 1981).

Characterization

This resulting material underwent Fourier Transform Infrared Spectroscopy (FTIR) analysis to confirm zeolite presence. X-ray Diffraction (XRD) was employed to scrutinize the crystallinity and structural composition of the synthesized materials while Scanning Electron Microscopy (SEM) provided detailed microscale imaging and surface characterization.

RESULTS AND DISCUSSION

The compositional analysis of Rice Husk Ash shows that (Table 1) the silica obtained after the chemical method was 91%. However, the composition of minerals leached from RHA is given in Table 1.

Table 1: chemical composition of rice husk ash determined by XRF

Chemical compositions	Wt.%
SiO_2	91.00
Al_2O_3	1.20
Fe_2O_3	1.28
K_2O	1.22
CaO	1.00
C	4.3

Table 2: Percentage of Zeolite obtained from RHA after impurities removal

	Weight of Silica (g)	Weight of Zeolite (g)	Percentage yield of zeolite (%)
RHA	8g	6.98g	87.25

FTIR Characterization

FTIR analysis was performed to examine the chemical bonding state and molecular structure of zeolite from rice husk. As an organic substance, it contains distinct classes of functional groups that were identified through comprehensive sample pretreatment and characterization. The identified functional groups were categorized into different sectors based on their respective spectral regions. In sector 1 (approximately 1500 -3000 cm^{-1}), the -O-H band at 2851 cm^{-1} and the bending vibration of adsorbed water molecules at 1659 cm^{-1}.

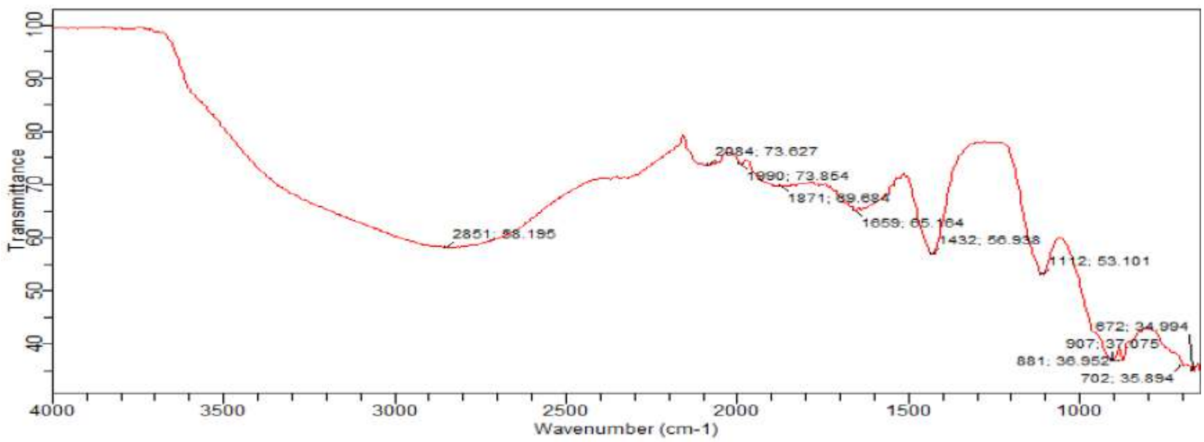

Figure 1: FTIR Characterization of the synthesized zeolite

Figure 1 exhibits a prominent peak at 950 cm^{-1}, attributed to asymmetric T-O stretching. Generally, T-O denotes a tetrahedral atom within the Si, Al framework, and its frequency may shift to a lower range with an increase in the number of tetrahedral Al atoms (Lee & Stebbins, 2006). Bands observed at 773 cm^{-1}, 690 cm^{-1}, and 571-460 cm^{-1} were predominantly associated with symmetric stretching, double-ring, and T-O bending vibrations, respectively. Lee and Stebbins, (2006), Matti and Surchi, (2014), reported that infrared (IR) spectrum of zeolite derived from rice husk reveals the presence of the 1223 cm^{-1} band, indicating the existence of pores with 3D channels. Additionally, bands at 455cm^{-1}, 542 $cm^{-1,}$ and 792 cm^{-1} provide insights into the overall crystalline structure of zeolite. Specifically, the IR absorption band at 455 cm^{-1} (I455) serves as an indicator of vibration units, while the band at 542 cm^{-1} (I542) is associated with the vibration of 5-membered oxygen rings.

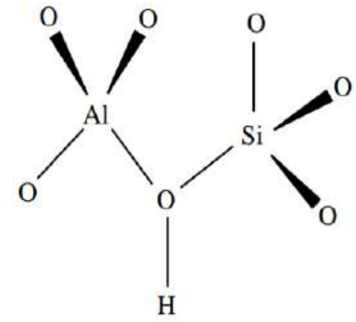

Figure 2: The unit block of a zeolite formed by the Si-O and Al-O bonds arranged in a tetrahedral configuration

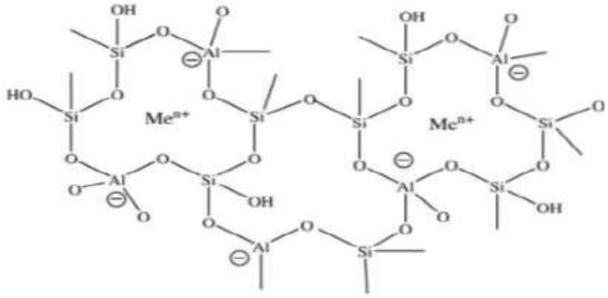

Figure 3: Illustration of the zeolites' framework structure in two dimensions denotes the presence of additional framework cations

XRD Analysis

X-ray diffraction (XRD) analysis was employed to assess the morphologies and crystallinity of the synthesized sample, focusing on Rice Husk ash. Microscopic observations revealed particle aggregates, indicating a highly amorphous nature. The XRD diffractograms, covering a 2theta range of 3° to 90°, demonstrated the amorphous nature of the samples, where each peak represented a distinct diffraction. Relative peak intensities were associated with sample crystallization levels, reflecting the type and position of atoms in the unit cell. Peak widths provided insights into crystallite size, indicating the crystalline quality of the sample.

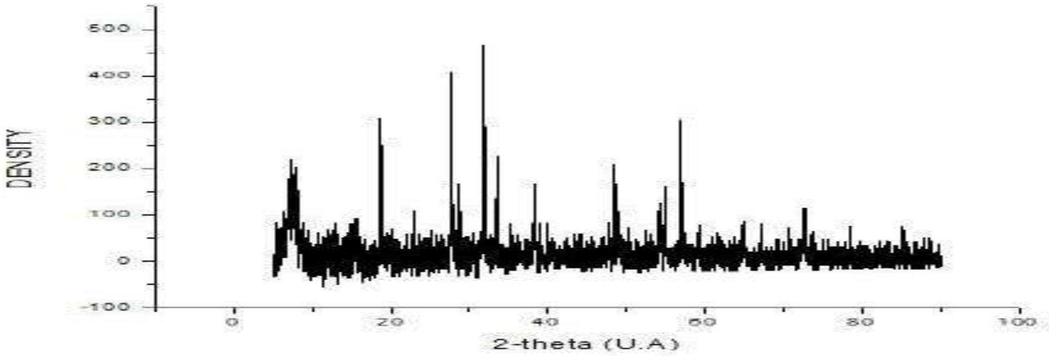

Figure 4: XRD Spectroscopy graph and energy peaks of Zeolites obtained

The XRD patterns of NaY zeolite synthesized from Rice Husk Ash silica samples at 80°C confirmed the formation of NaY zeolite. The major identification peaks on the XRD pattern for Rice husk Zeolite were located at 2θ = 12°, 19°, 28°, 34°, and 58°, while R. Peaks in the range of 2θ = 20–35° indicated degrees of crystallinity, suggesting the crystallization of amorphous silica material. The flat baseline in the XRD pattern further indicated the presence of highly crystallized zeolite. Notably, NaY zeolite synthesized from Rice husk exhibited a higher degree of crystallinity. The XRD patterns of the samples aligned with standard NaY zeolite, confirming their morphology as mentioned by (Salama et al., 2016) the zeolite phased presented at 2θ of 21.644° and 28.076°.

Scanning Electron Microscopy (SEM) of the Synthesize Zeolite

The microscopic view of the synthesized zeolite provides valuable insights into its structural characteristics and particle morphology. The images, depicted in Figure 4, reveal the presence of particle aggregates in zeolite. The observed aggregates offer visual evidence of the amorphous nature of the sample, contributing to a comprehensive understanding of their microstructure. The microscopic analysis further underscores the highly amorphous nature of the zeolite, aligning with the findings from the X-ray diffraction (XRD) analysis.

Figure 5: SEM View of Zeolites synthesized from Rice Husk

Additionally, the images captured through microscopic examination showcase the intricate details of particle distribution and arrangement within the zeolite structure. The presence of well-defined particle aggregates signifies the synthesis of zeolite and corroborates the identification peaks observed in the XRD patterns. These microscopic observations provide a crucial visual context to complement the structural and crystallinity information obtained from other analytical techniques, enhancing the overall characterization of the synthesized zeolite.

CONCLUSION

The FTIR results provide valuable insights into zeolites chemical bonding state and molecular structure. Analysis of various sample elements revealed a high concentration of silica oxide, accounting for 91.00% of the composition. The FTIR spectra highlighted characteristic bands at 1082.10 cm^{-1} and 806.27 cm^{-1}, associated with Si-O-Si stretching, confirming the presence of silicon in the sample and facilitating the characterization of zeolite. The band at 702 cm^{-1} indicates the stretching and bending of Al-O vibration.

In this study, we successfully synthesized pure and highly crystalline Zeolite NaY samples using readily available lignocellulosic materials (untreated Rice Husk). The outcomes confirmed the direct extraction of silica from these materials. Effective dissolution of silicon from Rice Husk was achieved through NaOH treatment at 80°C over a 24-hour incubation period. Importantly, the direct dissolution of silica-gel did not compromise the yield or quality of the final product. This simplifies the technological process and utilizes the heat generated during silica dissolution and acidification for hydrogel formation before thermal treatment. The silica content and Zeolite formation percentage ranged between 80% and 90%, indicating a positive and cost-effective Zeolite synthesis from rice husk waste. The presence of Zeolite crystals was corroborated by the XRD pattern, showing characteristic peaks at 2θ between 3 and 350, consistent with findings in previous literature studies. Exploring alternative uses for rice husk beyond combustion is recommended, such as utilizing it as a fuel source in power plants or incorporating it into building materials and concrete production. Controlled burning of rice straw can yield ashes suitable for applications like cement replacement and suspension agents for porcelain enamel. Avoiding uncontrolled burning is crucial to mitigate the suspension of silica in the atmosphere, preventing potential health hazards like silicosis. This research underscores the importance of sustainable management practices for agricultural residues like rice husk.

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