

Utilization of Bengkalis Beach Sand Silica as Raw Material in the Synthesis of Zeolite 4A

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Abstract

Zeolite 4A is a porous material that is widely used as an adsorbent, catalyst, membrane, ion exchanger, molecular sieve, etc. As a source of silica in the synthesis of zeolite 4A, silica from natural materials, biomass waste or chemicals has been used. In this research, silica extracted from Bengkalis beach sand (BBS) was used as raw material. The silica content in its oxide form, silicon oxide (SiO₂) in BBS reaches 90%. The synthesis of zeolite 4A was carried out using a hydrothermal process, by varying the mole ratio of Si/Al from the reactant sodium silicate to sodium aluminate, namely 1.2:1; 1.4:1; 1.6:1 at reaction temperatures of 100, 110 and 120°C. Based on characterization using X-ray diffraction and an infrared spectrometer, the best conditions were obtained at a mole ratio reactant of 1.6, a reaction temperature of 100°C with a crystallinity percentage reaching 80.97%. Based on SEM-EDX analysis, the zeolite has an agglomerated morphology with a Si/Al ratio of around 1.09. The surface area, pore volume, and pore diameter of the synthesized zeolite were analyzed using a Brunauer-Emmet-Teller (BET) technique, respectively 81.844 m²/g, 0.039 cm³/g, and 3.07 nm.

Keywords

Crystallinity, Bengkalis Beach Sand, Hydrothermal, Zeolite 4A

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1. INTRODUCTION

Silica sand is a type of natural sand that comes from quartz rock and has been broken into granular sand, generally containing high levels of silica (SiO₂). The silica in sand can be separated from impurities used as high-value chemicals or materials. Natural sand from Bancar Tuban contains around 71.3% silica, used in the synthesis of amorphous SiO₂ nanoparticles, a smart material that can be developed in drug delivery systems (Munasir, 2020). Silica nanopowders (NPs) in amorphous form have also been produced from natural silica sand found in Slopeng, Indonesia (Munasir, 2013). Utilizing silica from Tunisian sand, (Tounsi et al., 2009) synthesized Na-LTA zeolite using the hydrothermal method. Another source of silica sand is found in Bengkalis beach sand (BBS), Riau, Indonesia. Based on analysis using X-ray fluorescence (XRF) equipment, it was found that the silica content in the form of oxide (SiO₂) in BBS reached 90%. The results of the analysis, silica from BBS was used to make silica gel and sodium silicate. Sodium silicate synthesized from BBS silica, is used as raw material for making zeolite 4A using the hydrothermal method. The silica content of BBS has potential as a substitute raw material for commercial silica in synthesizing zeolite. Zeolite is an aluminum silicate material with a three-dimensional framework structure formed by tetrahedral [AlO₄]⁵⁻ and [SiO₄]⁴⁻

with pores filled with alkaline or alkaline earth metal ions and water molecules that can move freely (Moreira et al., 2018). Zeolite is composed of atoms (Al, Si), each of which is tetrahedral and connected by oxygen atoms in such a way as to form a three-dimensional framework. The composition of zeolite can be explained by three components as follows (Payra and Dutta, 2003):



Where,

$M_{n/m}^{m+}$ is the extra framework cation (metal element)
 $[Si_{1-n}Al_nO_2]$ explain the zeolite
 nH_2O which states the sorbed phase

Zeolite are classified as natural zeolite or synthetic zeolite (Derbe et al., 2021). Natural zeolite must be modified before use to increase its absorption capacity for organic pollutants, for example, used cationic surfactants (Supriyadi et al., 2021). Synthetic zeolite can be used by mimicking geological conditions, especially conditions that allow zeolite recrystallization. Zeolite 4A, one of the synthetic zeolites, is included in the zeolite type with a Linde Type A (LTA) framework (Garcia Mendoza, 2017). The zeolite 4A framework consists of cuboctahedral

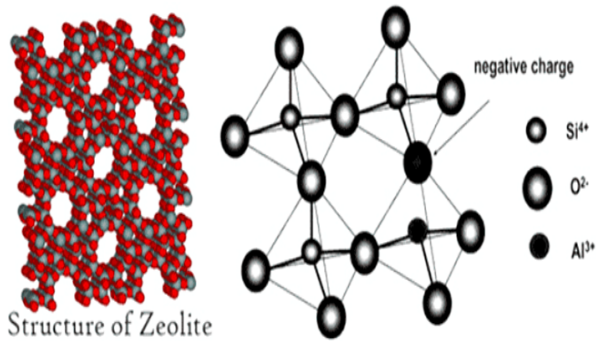
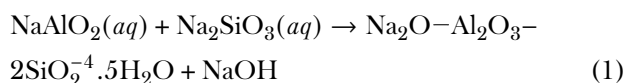


Figure 1. Zeolite Structure (Golomeova and Zendelska, 2016)

which has tetrahedral SiO_4^- on each edge of its framework. As a porous material, zeolite 4A has various uses, including water purification and toxic heavy metals removal (Rahman et al., 2018; Wu et al., 2018; Al-Jubouri et al., 2019), adsorbent (Wang et al., 2019), catalysts, ion exchange membranes, and molecular sieve (Ginting et al., 2019). The source of silica in the synthesis of zeolite 4A can come from kaolin (Du and Yang, 2010; Li et al., 2010; Omisanya et al., 2012; H Kareem et al., 2014; Golbad et al., 2017; Garcia Mendoza, 2017; Du and Yang, 2010; Rahman et al., 2018; Mgbemere et al., 2019; Wang et al., 2019; Dahani et al., 2020; Sowunmi et al., 2022) sugar cane bagasse, rice husks, coal bottom ash (CBA), coal fly ash (CFA), natural zeolite (Ginting et al., 2019), basalt rock (Hwang et al., 2018), opal waste rock (Wu et al., 2018), bauxite (Rahman et al., 2021), from chemicals (Menad et al., 2016; Paprica et al., 2022) and waste sludge from water treatment plants (Wongwichien et al., 2014). In this research, the silica extracted from BBS was used as raw material for making zeolite 4A. The use of beach sand is expected to increase the economic value of sand, which was previously only used as a building material. The synthesis stage begins with making sodium silicate by melting the extracted silica sand with NaOH. In previous research, NaOH was used in the alkali fusion process to melt silica sand. The industrial alkali fusion process mostly uses Na_2CO_3 , carried out at temperatures above 1200°C (Owoeye et al., 2021). The most common synthesis of 4A zeolite is to be used by the hydrothermal method (Al-Jubouri et al., 2019; Cui et al., 2018; Ginting et al., 2019; Golbad et al., 2017). The zeolite synthesis stage uses a hydrothermal process, two factors that influence the zeolite synthesis are varied, the reactant mole ratio and the reaction temperature. The mole ratio of Si/Al reactants used is 1.2:1; 1.4:1 and 1.6:1 with hydrothermal reaction temperatures at 100, 110, and 120°C . The chemical reaction of zeolite 4A crystallization in the hydrothermal process in general is:



Hydrothermal processes involve modifying the texture or structure of a solid, which follows the laws of thermodynamics and reduces the free energy of the system (Byrappa and Yoshimura, 2012).

Hydrothermal techniques are quite popular synthesis techniques due to their simplicity and low cost. The resulting is commonly well-crystallized and chemically homogeneous (Azis et al., 2015).

2. EXPERIMENTAL SECTION

2.1 Materials

Bengkalis beach sand (BBS) as a source of silica (SiO_2), solid NaOH Merck, $\text{Al}(\text{OH})_3$ Merck, HCl 32% Merck, distilled water, filter paper, and aluminum foil.

2.2 Silica Extraction from Bengkalis Beach Sand

Approximately 100 grams of clean and fine Bengkalis beach sand ($75\mu\text{m}$), was put into a glass beaker and extracted (leaching) with 300ml 3M HCl for 3×8 hours. The resulting silica was washed with distilled water and dried in an oven. The constituent mineral content of sand, as a source ingredient of sodium silicate, was analyzed using X-ray fluorescence (XRF) and X-ray diffraction (XRD) equipment.

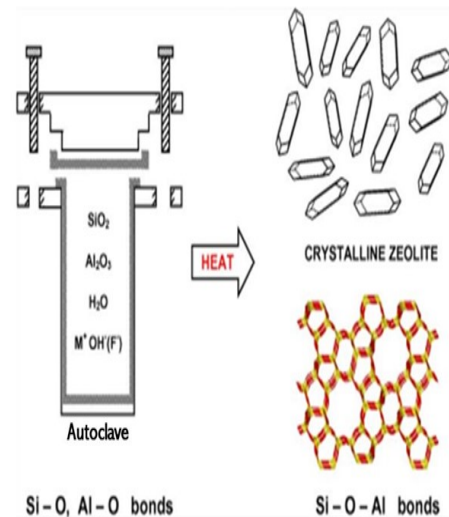


Figure 2. Hydrothermal Reaction Process (Sumaria and Govindasamy, 2014)

2.3 Hydrothermal Synthesis of Zeolite 4A

The sodium aluminate solution was added slowly to the sodium silicate solution according to the desired Si/Al ratio, namely 1.2:1; 1.4:1, and 1.6:1. The resulting mixture is like a white gel. The mixture was then transferred into a Teflon autoclave for hydrothermal processing at varying temperatures of 100, 110, and 120°C for 3 hours. White zeolite was produced after washing with distilled water. The white zeolite solid was dried at 110°C for structural analysis.

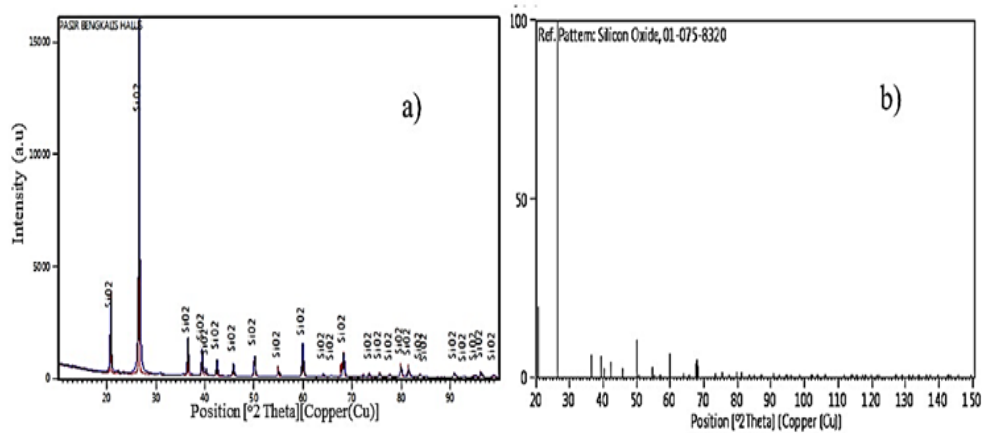


Figure 3. X-ray Diffraction Pattern: a) Silica and from Bengkalis Beach b) Silicon Oxide Standard

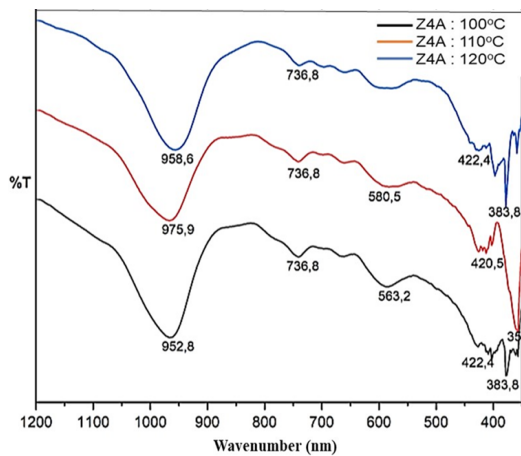


Figure 4. FTIR Spectrum of Synthesized Zeolite at a Ratio of 1.6 with Temperature Variations

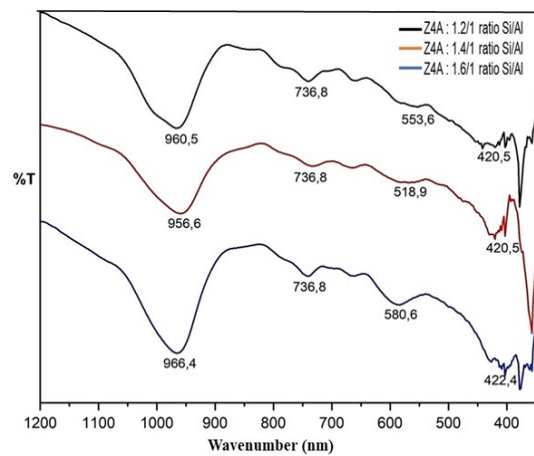


Figure 5. FTIR Spectrum of Zeolite Synthesis Results at 100°C with Variations in the Si/Al Ratio

2.4 Synthesis Results of Zeolite Structure Analysis

The silica content and structure in the silica sand raw material were analyzed using XRF and XRD equipment. The synthesized zeolite was analyzed using FTIR, XRD, and SEM-EDX equipment, and surface area using the BET test.

3. RESULTS AND DISCUSSION

3.1 Silica Sand Analysis

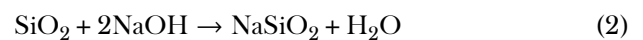
Analysis of Bengkalis Beach sand (BBS) using XRF equipment, aims to determine the composition of the BBS components. Based on XRF analysis, the silica content in BBS resulting from leaching with 3M HCl solution increased from 89.102% to 93.110%. The results of XRF analysis of BBS before and after the leaching process are shown in Table 1.

An increase in silica levels can occur due to impurity in the sand in the form of minerals Al, Fe, Ca, K, Ti, etc., dissolved in the HCl solution, while silica cannot dissolve in HCl. The sand

resulting from leaching was then analyzed using XRD, and a spectrum pattern was obtained that was identical to the silicon oxide standard ICDD 01-075-8320, as shown in Figure 3.

The zeolite 4A was synthesized hydrothermally using silica sand from the leaching process and was added to NaOH solution at 500°C to form sodium silicate. The melting temperature was used at 500°C considering that the melting point of NaOH is at 318°C so at this temperature NaOH completely dissociates to form Na⁺ and OH⁻ ions.

The reaction that occurs in the process of melting silica with NaOH is as follows (Zaky et al., 2008):



3.2 Characterization of Zeolite 4A

The bonds between atoms and functional groups in the synthesized zeolite 4A were determined using a Fourier Transform InfraRed (FTIR) spectrophotometer. From the three varia-

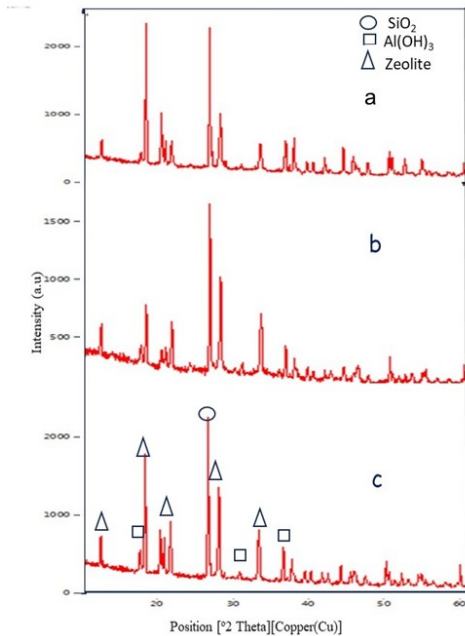


Figure 6. X-ray Diffraction Pattern of Synthesized Zeolite with Mole Ratio: a) 1.2:1 b) 1.4:1 c) 1.6:1

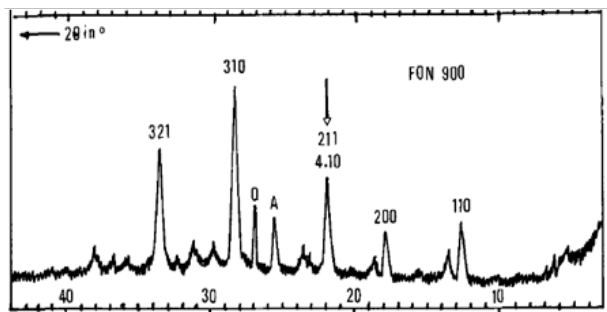


Figure 7. Standard 4A Zeolite Diffractogram (Murat et al., 1992)

tions of mole ratio and temperature used, an FTIR spectrum pattern was obtained, as shown in Figure 4.

The characteristic FTIR spectrum for 4A zeolite was by the appearance of absorption bands at $1250\text{--}950\text{ cm}^{-1}$ for the asymmetry of the tetrahedral TO4 bond, $750\text{--}650\text{ cm}^{-1}$ for the bond symmetry range (T=Si or Al) (Wu et al., 2018). Meanwhile, absorption at wave numbers $650\text{--}500\text{ cm}^{-1}$ is for polyhedral double ring vibrations, $500\text{--}420\text{ cm}^{-1}$ indicates TO4 bond bending vibrations and absorption at $420\text{--}300\text{ cm}^{-1}$ indicates the presence of open pores in zeolite 4A (Ginting et al., 2019). The FTIR spectrum analysis results were also found for the three variations in the Si/Al reactant mole ratio (Figure 5). Several main absorptions for the zeolite framework were also found in the three spectra, such as the asymmetry range of the tetrahedral TO4 bond at wave numbers $1250\text{--}950\text{ cm}^{-1}$ and the symmetry range for T–O bonds at wave numbers $750\text{--}650$

Table 1. XRF Results Analysis of Bengkalis Beach Sand

Composition	Concentration (%) Before Leaching	Concentration (%) After Leaching
Al ₂ O ₃	3.596	3.105
SiO ₂	89.102	93.110
P ₂ O ₅	2.826	0.836
K ₂ O	0.910	0.429
CaO	1.627	0.604
TiO ₂	0.336	0.195
Cr ₂ O ₃	0.002	0.001
MnO	0.016	0.008
Fe ₂ O ₃	1.303	0.598
ZnO	0.003	0.001
SrO	0.007	0.003

cm^{-1} (T=Si or Al).

The resulting FTIR spectrum pattern is very similar in all synthetic variations, however, the zeolite made with a molar ratio of 1.6:1 at a temperature of 100°C has a higher transmittance intensity at wave numbers of $650\text{--}500\text{ cm}^{-1}$ and $500\text{--}420\text{ cm}^{-1}$. The absorption intensity ratio at wave numbers $(500\text{--}420)/(650\text{--}500)$ can be used to estimate zeolite crystallinity. This also shows the number of double rings formed from the zeolite framework.

Characterization using X-ray diffraction was carried out on the synthesized zeolite at a temperature of 100°C with mole ratios 1.2:1, 1.4:1, and 1.6:1, were shown in Figure 6.

The XRD spectrum pattern of the synthesized zeolite matches well with the standard zeolite 4A spectrum (Figure 7) (Murat et al., 1992) which confirms that zeolite 4A has been successfully synthesized. The sharp peaks of zeolite 4A occur in the three synthesized XRD spectra at 2θ : 12.5° , 18° , 21.7° , 28.1° , 33.8° .

However, several other peaks were found in the three synthesized zeolites. From the analysis results, SiO₂ and Al(OH)₃ peaks were found in the products. Silica sand from Bengkalis Beach, containing silicon oxide with a quartz phase (2θ angle: 26.6°), was still found mixed with zeolite 4A in all three XRD spectra. Melting the silica with alkali other than NaOH, such as Na₂CO₃ (Owoeye et al., 2021), will reduce the impurities. From the crystallinity analysis, zeolite synthesized with a molar ratio of 1.6:1 at a temperature of 100°C has a crystallinity of 80.97%. One of the factors that influences the final result of the zeolite synthesis process is the ratio of Si and Al reactants. Increasing the ratio or ratio of constituent substances will affect the composition of the resulting zeolite framework and the speed of crystallization.

The SEM-EDX morphology of the zeolite made at a temperature of 100°C with a mole ratio of 1.2:1; 1.4:1 dan 1.6:1 was studied as shown in Figure 8. The morphology of the resulting zeolite looks like an agglomerate but with a homogeneous size distribution. Wang et al. (2019) reported that

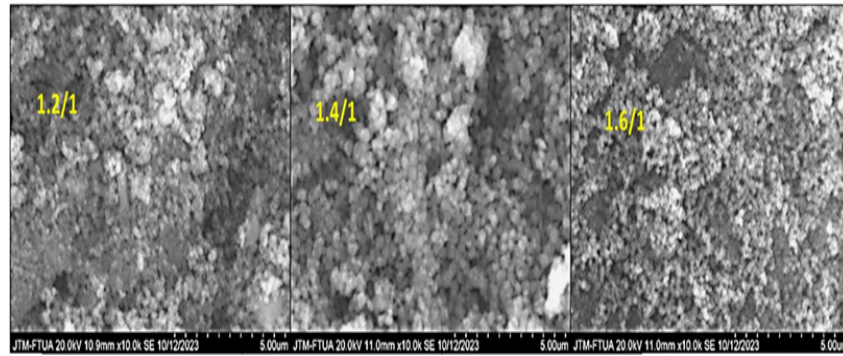


Figure 8. SEM Image of Synthesized Zeolite at 100°C, Si/Al Ratio 1.2:1 : 1.4:1 and 1.6:1 with Magnification 10000x

Table 2. Percent Crystallinity of Zeolite 4A at Various Mole Ratios

Ratio Si/Al	% Crystallinity
1.2:1	69.34
1.4:2	75.13
1.6:1	80.97

Table 3. EDX analysis results of synthetic zeolite at a mole ratio of 1.6:1

Element	Weight (%)	Atomic (%)
C K	41.91	50.80
O K	47.32	43.06
Na K	4.29	2.72
Al K	3.04	1.64
Si K	3.43	1.78
Totals	100.00	

zeolite 4A crystals synthesized from kaolin were cube-shaped according to commercial zeolites. From the SEM photo, it can be seen that the particle size of zeolite with a molar ratio of 1.6:1 is smaller than a molar ratio of 1.2:1 or 1.4:1.

Based on EDX analysis, the Si/Al ratio of zeolite made with a Si/Al ratio of 1.6 at a hydrothermal temperature of 100°C is 1.09. Zeolites can be categorized by the Si/Al ratio, so zeolites synthesized from BBS are included in the low silica zeolites group because Si/Al = 1-2. The results of the EDX analysis of the synthesized zeolite with a mole ratio of 1.6:1 at a hydrothermal temperature of 100°C are shown in Table 3.

Surface area analysis of the product using the BET method obtained a surface area of zeolite 4A of 81.844 m²/g and a specific surface area of 647.5 m²/g. Meanwhile, the pore structure resulting from the BJH method shows a pore diameter of 3.07 nm and a pore volume of 0.039 cm³/g, including the mesopore group, because the pore diameter was around 2-50 nm.

4. CONCLUSION

Hydrothermal synthesis of zeolite 4A was carried out using silica extracted from Bengkalis Beach sand (BBS). By varying the hydrothermal temperature and the Si/Al reactant mole ratio, zeolite 4A was obtained, a porous material belonging to the mesopore group. Analysis using X-ray diffraction showed that the synthesized zeolite matched with standard zeolite. The best results in reaction conditions with a mole ratio of 1.6 at a hydrothermal temperature of 100°C. From the SEM-EDX analysis, the zeolite has an agglomerated morphology. However, the silica phase was still found in the synthesized zeolite. This phenomenon can happen because, in raw materials, silica was also found in the form of quartz crystals. The alkali fusion process using various alkalis is needed to minimize the presence of silica in the zeolite.

5. ACKNOWLEDGMENT

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