SYNTHESIS OF NaP1 AND FAUJASITE ZEOLITE FROM NATURAL ZEOLITE OF ENDE-NTT AS LEAD (Pb(II)) ADSORBENT

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ABSTRACT

Synthesis of zeolite from Ende-Nusa Tenggara Timur (NTT) natural zeolite was conducted using the hydrothermal method, both with and without the addition of Na_2SiO_3 and NaAlO_2 . This research was conducted to produce synthetic zeolite utilized to remove lead (Pb(II)) through the adsorption process. The temperature of crystal formation (aging) was performed at 60°C for 6 hours, and the hydrothermal process was at 100°C for 24 hours. The resulting synthetic zeolite included the NaP1 and faujasite types. The effects of adsorption parameters, such as pH and contact time, were identified. The best adsorption capacity was demonstrated by synthetic zeolite without the addition of Na_2SiO_3 and NaAlO_2 , with a value of 144.7191 mg/g at pH 4, with a 45 minute contact time. The results showed that the synthesis of zeolite performed by the hydrothermal method could increase the cation exchange capacity (CEC) up to 105.42 cmol/kg , from a natural zeolite with a CEC of 20.14 cmol/kg . The Langmuir model was consistent with an isothermal adsorption equilibrium process, and the adsorption free energy (ΔG_{ads}) was consistent with physical adsorption (physisorption). The NaP1 zeolite of Ende-NTT natural zeolite was a better Pb(II) heavy metal adsorbent than the synthetic zeolites of fly ash and coal bottom ash.

Keywords: Adsorption, Adsorption Free Energy (ΔG_{ads}), CEC, Hydrothermal, Zeolite

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INTRODUCTION

Water pollution caused by heavy metals continues to be a major issue faced today. Heavy metals are dangerous pollutants in industrial process wastes from metallurgy, oil refining, pesticide production, paint, and battery industries¹. The problem of pollutants, in forms of heavy metals, is more severe than that of organic pollutants due to the toxicity of heavy metal ions on organisms and the difficulty in dissolving them biologically and chemically. Lead (Pb(II)) is one of the problematic heavy metal pollutants.

A number of efforts have been made to reduce the concentration of toxic metals in the environment, one of which is by using the adsorption method. It is frequently chosen due to its accessible, energy-efficient, and effective operation². One of the most commonly used adsorbents in waste treatment (of heavy metals like Pb(II)) is natural zeolite³. The use of natural zeolite as an adsorbent is due to its simple method, raw material availability in nature, adequate adsorption capacity to control air and heavy metal pollution. In Indonesia, abundant natural zeolite is found and spread in several areas, one of which is in Ende-Nusa Tenggara Timur (NTT).

In general, natural zeolite has high Si/Al ratios and contains impurities. These factors greatly reduce the Cation Exchange Capacity (CEC) and limit the application of natural zeolite⁴. Various efforts have been made to increase the adsorption capacity of natural zeolites, one of which is by using the hydrothermal method and changing the ratio of Si/Al in order to more closely resemble synthetic zeolites. Synthetic zeolites have high crystallinity and catalytic activity and contain minimum metal oxide impurities⁵. However, synthetic zeolites have high production cost⁶, and are not resistant to high temperature⁷. Meanwhile, natural zeolites have low crystallinity and catalytic activity as they contain a large number of metal oxide impurities, and diverse pore sizes⁸, but have good thermal stability⁹. A large Si/Al ratio value

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indicates positive charge and results in smaller cation exchange capacity of a zeolite, while a small Si/Al ratio indicates a negative charge and a greater cation exchange capacity of a zeolite¹⁰.

This research conducted a synthesis of zeolite from Ende-NTT natural zeolite by using the hydrothermal method with varied concentrations of Na_2SiO_3 and NaAlO_2 . In addition, in accordance with the increased adsorption capacity of methylene blue from synthetic zeolites resulting in an increase in adsorption capacity by 46.7% and CEC by 16%¹¹, tests were conducted to observe the effects of produced synthetic zeolite on Pb(II) heavy metal adsorption.

EXPERIMENTAL

Natural Zeolite Preparation and Activation

The natural zeolites were ground and sieved into powder with the required sieve size of 200 Mesh and heated in a 300 °C furnace for 3 hours, to give unactivated natural zeolite (Z). Furthermore, they were chemically activated by mixing in 3 M HCl and 3 M NaOH solutions, to give activated natural zeolite ZA and ZB, respectively. Then, the natural zeolites, both before and after activation, were further characterized by XRD, SEM, and FTIR.

The Synthesis of Zeolite Using Hydrothermal Method with or without the Addition of Na_2SiO_3 and NaAlO_2

Unactivated natural zeolite (Z) samples with a total weight of 7 grams were added with 25 mL of 2 M, 2.5 M, 3M, and 3.5 M NaOH. The aging process consisted of heating the mixtures at 60°C for 6 hours, to initiate the process of crystalline nuclei formation. Then the hydrothermal process consisted of heating the mixtures at 100°C for 24 hours. After hydrothermal treatment, the crystallized solids were characterized by XRD to identify the sample conditions and optimum NaOH concentration for the hydrothermal synthesis process. The same procedure was done for base and acid activated zeolite.

The reaction condition that yielded a synthetic zeolite with the highest crystallinity value was then used in the synthesis of zeolite with the addition of silicate and aluminate. In this case, the best result was shown by base-activated zeolite (ZB) with the concentration of NaOH of 3M. The above procedure then repeated by reacting ZB with the addition of Na_2SiO_3 or NaAlO_2 , and 3M of NaOH. After the hydrothermal treatment, the crystallized solids of synthetic zeolites, ZS (from unactivated zeolite), ZSA (from acid-activated zeolite), and ZSB (from base-activated zeolite), were characterized by XRD, SEM, and FTIR.

Determination of Lead (II) Optimum Adsorption Parameters

A total of 0.05 grams of zeolite adsorbent was mixed with 50 mL of Pb(II) solution at a concentration of 200 mg/L. The mixture was shaken, and subsequently, the mixture was centrifuged for 15 minutes, and the Pb(II) content in the filtrate was analyzed by using AAS. The adsorption was observed based on two parameters, pH and contact time. The pH of Pb(II) solutions used was 2, 4, and 6. While the contact time applied was 15, 30, 45, 60, 75, 90, 105, 120, and 135 minutes. To maintain the pH of the solutions, 0.1 M NaOH or 0.1 M HNO_3 was added before the adsorption.

CEC (Cation Exchange Capacity) Determination

A total of 0.1 grams of zeolite was added to 10 mL of 0.5 M CaCl_2 solution and saturated for 24 hours. The solution was separated by centrifugation for 15 minutes. The supernatant was removed, and the pellets were then washed using 80% ethanol until chloride free. The chloride-free pellets were further extracted to obtain the calcium absorbed in the zeolite samples. The extraction was performed using 10 mL of 1 M NH_4Cl for one hour. The extraction process was repeated for 5 times. The collected extract was then mixed with 1 M NH_4Cl up to 100 mL of volume. Then the calcium was measured using AAS.

Determination of Adsorption Isotherm

A total of 0.05 grams of zeolite adsorbent was added to 50 mL of Pb(II) solution at concentrations of 100, 150, 200, 250, 300, 350, and 400 mg/L at the optimum pH and then agitated using the optimum contact time. Subsequently, the mixtures were centrifuged for 15 minutes, and the Pb(II) content in the filtrates was analyzed using AAS.

RESULTS AND DISCUSSIONS

The results of XRD analysis conducted on Ende-NTT natural zeolite (Z) are shown in Fig.-1. The figure highlights that the natural zeolite is mixture of mordenite and clinoptilolite zeolites as they have

characteristic peaks at the angle of 2θ in accordance with JCPDS database. The activation treatment in this study was conducted chemically by adding 3 M NaOH (base activation) and 3 M HCl (acid activation). The activation of the natural zeolite aimed to remove the impurities. The results of XRD analysis conducted on Ende-NTT natural zeolite after the activation process are shown in Fig.-1. Figure-1 indicates that the activation treatment with 3 M NaOH and 3 M HCl did not significantly change the diffractogram peak due to the relatively stable natural zeolite structure because the natural zeolites contain a high amount of metal oxides providing resistance in the basic structure of the zeolite¹¹.

Fig.-1: Diffractogram of Ende-NTT Inactivate Natural Zeolite (Z), 3 M NaOH Activation (ZB), and 3 M HCl Activation (ZA)

NaOH acts as a dissolving activator for the Si and Al contained in the zeolite samples. Na^+ cations also holds an important role in zeolitization in which the production of water-soluble sodium silicate is higher, so that the crystallizing process in synthetic zeolite formation becomes faster¹². The hydrothermal method aimed to produce zeolites with high purity and good thermal properties more resistant to heat. The crystallinity of the synthetic zeolites at various concentrations of NaOH is shown in Table-1. Table-1 shows that the optimum NaOH concentration for the synthesis of zeolite by the hydrothermal method is 3 M in zeolites with base activation (3 M ZSB), as they have the highest crystallinity degree of 64.66%. The high degree of crystallinity evidenced in the 3 M ZSB (ZSB0) zeolite sample, which was synthesized with 3 M NaOH, indicates that its structure is more organized than other zeolite samples.

Table-1: Crystallinity of Synthetic Zeolites on varied NaOH Concentrations

Sample	Crystallinity Degree (%)
2 M ZS (2 M NaOH)	56.9
3 M ZS (3 M NaOH)	53.06
2 M ZSA (2M NaOH)	63.21
3 M ZSA (3 M NaOH)	63.87
2 M ZSB (2 M NaOH)	63.54
3 M ZSB / ZSB0 (3 M NaOH)	64.66
3.5 M ZSB (3.5 M NaOH)	59.92

The synthesis process of zeolites by adding different amounts of Na_2SiO_3 and NaAlO_2 was conducted using the synthesis conditions for ZSB0 synthesized with 3 M NaOH. Na_2SiO_3 and NaAlO_2 were added to

provide other sources of silica and alumina; thus, eventually changing the Si/Al ratio of the zeolite products. The results of XRD analysis performed on the synthesized zeolites by the hydrothermal method of Ende-NTT natural zeolite, either with or without the addition of Na_2SiO_3 , and NaAlO_2 are shown in Fig.-2. Figure-2 shows that the synthetic zeolites of ZSB0, ZSBSi10, ZSBSi20, ZSBA110, and ZSBA120 are mixtures of NaP1 and faujasite types of zeolites as they have characteristic peaks at the angle of 2θ in accordance with the JCPDS database. The best-synthesized zeolite with the addition of Na_2SiO_3 and NaAlO_2 variation was the one from the addition of 20 mL Na_2SiO_3 (ZBSi20) due to its highest percent crystallinity of 75.11 %. Figure-2 also shows that ZBSi20 is dominated by faujasite type zeolite. Addition of silicate resulted in more dominate faujasite-type zeolite, as shown by the increase of the intensity of peak at $2\theta(^{\circ})$ of 26.6677. In contrast, the addition of aluminate resulted in a more dominate NaP1 type zeolite, as shown by a peak at $2\theta(^{\circ})$ of 28.0813.

The results of SEM analysis performed on Z and ZSBSi20 are shown in Fig.-3. Figure-3a shows the morphology of the natural zeolite, a mixture of mordenite and clinoptilolite. The zeolite was not in a granule form, instead, the two types zeolite were attached. Figure-3b also shows a mixture of zeolites NaP1 and faujasite. The NaP1 looks more like thin plates stuck together in granules, while the faujasite had ortho rhombic structure. Faujasite consist of two types of zeolite, the X and Y types of zeolite, with Si/Al ratio of 1-1.5 and 2.5, respectively¹³. Meanwhile, the NaP1 has the Si/Al ratio of around 2.3¹⁴.

Fig.-2: Diffractogram of Synthetic Zeolite without the Addition of Na_2SiO_3 and NaAlO_2 (ZSB0), with Additions of 10 mL Na_2SiO_3 (ZSBSi10), 20 mL Na_2SiO_3 (ZSBSi20), 10 mL NaAlO_2 (ZSBA110), and 20 mL Na_2SiO_3 (ZSBA120)

FTIR spectrum analysis was performed to identify the functional groups in the natural and synthetic zeolites. The results of the Z, ZSB0, and ZSBSi20 FTIR are shown in Fig.-4. It shows that the range of O-Al-O or O-Si-O symmetry on the internal tetrahedral structure of the Z, ZSB0, and ZSBSi20 appeared respectively in bands at 693, 694, and 694 cm^{-1} , while for external linkages appeared respectively in bands at 796, 778, and 778 cm^{-1} . Si-O or Al-O folds in the Z, ZSB0, and ZBSi20 appeared respectively in bands at 461, 436, and 441 cm^{-1} , while the asymmetric range of Z, ZSB0, and ZBSi20 appeared respectively in bands at 1041, 1015, and 1029 cm^{-1} . The synthesis process either with or without the addition of Na_2SiO_3 and NaAlO_2 had no effect on the functional groups of the zeolites as the synthetic

zeolite absorption band is still located in the main area of the tetrahedral bonds of the main zeolite components (SiO_4^{4-} and AlO_4^{5-}) include the band emergence in the symmetry range of O-Al-O or O-Si-O in the internal tetrahedral region at $650\text{--}720\text{ cm}^{-1}$; while for the external linkage, the band will appear in the region at $750\text{--}820\text{ cm}^{-1}$. The symmetric-O or Al-O will appear in the region of $420\text{--}500\text{ cm}^{-1}$, while absorption in the region of $950\text{--}1250\text{ cm}^{-1}$ indicates an asymmetric range¹⁵.

Fig.-3: Surface Morphology of ZA (a) and ZSBSi20 (b)

Fig.-4: Spectrum of FTIR Z (—), ZSB0 (—), and ZSBSi20 (—)

Optimization of adsorption parameters of Pb(II) metal ion by ZSB0 and ZSBSi20 adsorbents were performed by varying pH and contact time. The optimum pH for ZSB0 and ZSBSi20 adsorbents in Pb(II) metal ions adsorption occurred at pH 4 with respective adsorption capacities of 124.4064 and 90.3279

mg/g (Fig.-5). Meanwhile, the optimum contact time for ZSB0 and ZBSi20 adsorbents was 45 and 105 minutes with respective adsorption capacities of 144.7191 and 125.1530 mg/g (Fig.-6a and 6b). This result is better than the adsorption of Pb(II) metal ions by using NaP1 zeolite from fly ash with a maximum adsorption capacity of 0.98 mg/g¹⁶ and NaP1 zeolite from coal bottom ash with a maximum adsorption capacity of 15.4 mg/g¹⁷.

Fig.-5: Adsorption Capacity of ZSB0 and ZBSi20 on Pb(II) Metal Ion at varied pH

Fig.-6: Adsorption Capacity of ZSB0(a) and ZBSi20 (b) on Pb(II) Metal Ion at varied Contact Time

One common indicator to identify the quality of zeolites before and after the synthesis process is to measure the ion exchange capacity, known as CEC. The CEC of natural zeolite and synthetic zeolite is shown in Fig.-7. Figure-7 shows that the process of chemical zeolite activation and hydrothermal synthesis can increase CEC. The increase of CEC through the activation process and hydrothermal synthesis caused by this treatment has cleared the zeolite pore space of water molecules and metal oxides, as well as produced zeolite with high crystallinity enabling zeolite activity to increase¹⁸. In addition to the removal of the metal oxides covering the exchange area and increasing the pore size, the hydrothermal synthesis process can also lead to the transformation process of natural zeolite into a type of synthetic zeolite with better quality¹⁹.

The determination of adsorption isotherm was performed to determine the relationship between adsorbate concentration and absorption rate at the adsorbent surface at room temperature and optimum condition, as well as the interaction between adsorbent and adsorbate. The data results of Pb(II) metal ion isotherm

adsorption by ZSB0 and ZSB Si20 were analyzed by using two adsorption isotherm models: the Langmuir and Freundlich models.

Fig.-7: Natural Zeolite and Synthetic Zeolite CEC

Based on the linear equations obtained from the Langmuir and Freundlich isotherm adsorption curves, the values of isotherm parameters including R^2 , q_m , K_L , R_L , K_F , and n were determined. The isotherm parameter values of Pb(II) metal ion adsorption by ZSB0 and ZSB Si20 are shown in Table-2.

Table-2: Adsorption Isotherm Parameter of Pb(II) Metal Ion by ZSB0 and ZSB Si20

Isotherm	Parameter	ZSB0	ZSB Si20
Langmuir	R^2	0.9494	0.9925
	q_m	181.8181	85.4701
	K_L	0.7639	0.3939
	R_L	0.0129	0.0247
Freundlich	R^2	0.7088	0.6461
	K_F	79.5976	47.2933
	n	0.2052	0.1211

Table-2 highlights the adsorption of Pb(II) metal ions by ZSB0 and ZSB Si20 entailing the Langmuir isotherm model, for it provides a fairly high correlation coefficient (R^2) respectively of 0.9494 and 0.9925, followed by the Freundlich isotherms respectively of 0.7088 and 0.6461. This shows that the adsorption process is dominated by monolayer adsorption (homogeneous). The Langmuir isotherm describes adsorption on one active side in which once a molecule occupies an active site, there will be no further absorption, and if the adsorbent active site is saturated with adsorbate, increased adsorbate concentration does not elevate the amount of adsorbed Pb(II) metal ions²⁰.

Other parameters utilized to determine the adsorption process were the values of q_m , K_L , and R_L . The q_m value represents the maximum theoretical adsorption capacity. K_L value indicates the capacity of the adsorbate molecular bond on the adsorbent. The value of R_L is an equilibrium parameter or an adsorption dimension stating that $R_L > 1$ value indicates poor adsorption process, $R_L = 1$ value indicates the linear adsorption process, $0 < R_L < 1$ value indicates beneficial adsorption process, and $R_L = 0$ indicates that the adsorption process is irreversible²¹. Table-2 shows the q_m and K_L values in ZSB0 were higher than in ZSB Si20, whereas the R_L values of ZSB0 and ZSB Si20 were in the range of $0 < R_L < 1$. This indicates that

the ZSB0adsorbent is better for use as a Pb(II) metal ion adsorbent compared with the ZSBSi20 adsorbent.

The value of adsorption-free energy (ΔG_{ads}) was also examined to determine the nature of the adsorption process. The values of ΔG_{ads} up to -20 kJ/mol are consistent with physical adsorption (physisorption), whereas ΔG_{ads} values above -40 kJ/mol are consistent with chemical adsorption (chemisorption)²². The results of ΔG_{ads} calculation in this research showed that the value of ΔG_{ads} for ZSB0 samples is -9.0874 kJ/mol, and that for ZSBSi20 samples is -7.6464 kJ/mol. Hence, the ZSB0 and ZSBSi20 adsorbents in Pb(II) metal ions adsorption have physical adsorption properties (physisorption).

Physical adsorption (physisorption) occurs when the intermolecular force is greater than the attraction force between the molecules or the relatively weak attraction force between the adsorbate and the adsorbent surface. This force is called the Vander Waals force, so that the adsorbate can move from one surface to another part of the adsorbent²³. The force between molecules is the attraction between the fluid molecules and the solid surface, while the intermolecular force is the attraction among the fluid molecules.

CONCLUSION

The synthesis process succeeded in producing NaP1 and faujasite types of synthetic zeolites. The two best synthetic zeolites, ZSB0 and ZSBSi20, were used in the adsorption of Pb(II) metal ion. The optimum conditions for the Pb(II) metal ion adsorption by the ZSB0 was obtained at pH 4 for 45 minutes, which is more efficient compared to the ZSBSi20. The synthetic zeolites were shown to have higher CEC than the natural zeolite. The adsorption process of Pb(II) metal ions by the synthetic zeolites ZSB0 and ZSBSi20 followed the Langmuir isotherm model and had physical adsorption properties (physisorption).

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