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Modification of Lampung and Bayah Natural Zeolite to Enhance the Efficiency of Removal of Ammonia from Wastewater

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In this research, modification of Lampung and Bayah natural zeolites was carried out to increase the zeolite's capacity as an ammonia adsorbent. Natural zeolite is modified by acid treatment using 6 M HCl and ion exchange using 1 M NH_4NO_3. The modification process continued with calcination at 500 °C for 4 h. X-ray fluorescence characterization shows changes in composition in the modified zeolites. The significant increase in the Si/Al ratio occurred in the modified zeolite with acid treatment that is 10.03 for Lampung natural zeolite HCl (LNZH) and 9.20 for Bayah natural zeolite HCl (BNZH). Surface area increases due to increasing Si/Al ratio. FTIR results indicate changes in the intensity of hydroxyl groups and $pyrH^+$ as a result of the increase in total acidity of zeolites. The zeolites performance test proves that the Bayah natural zeolite has a higher ammonia adsorption capacity than Lampung natural zeolite. Ion exchange-modified zeolite has a higher ammonia adsorption capacity than zeolite modified with acid treatment.

Keywords: Natural zeolite, Zeolite modification, Ammonia adsorption, Wastewater.

INTRODUCTION

Ammonia is one of the most widely produced inorganic chemicals because of its use in commercial industries, such as the production of medicines, cleaners and fertilizers [1]. Ammonia waste from the remaining production of these products will have a negative impact if not treated properly.

Excessive nitrogen content from ammonia waste is a nutrient source for aquatic plants, resulting in uncontrolled growth which results in eutrophication and disruption of ecosystem [2]. Excessive amounts of ammonia in the environment also cause negative effects to humans. At concentrations more than 300 ppm ammonia can cause death [3].

The processing of ammonia can be performed by several methods. One method that is quite effective, simple and inexpensive to treat ammonia waste is the adsorption method. Ammonia adsorption process uses adsorbent material that can absorb ammonia so that the concentration in the solution decreases. In the literature there are several types of adsorbents which have been studied for ammonia adsorption, namely activated carbon, zeolite, alumina, silica and graphene oxides [4].

Zeolite is an aluminosilicate-based micropore material commonly used as an adsorbent and catalyst. These aluminosilicates have high crystallinity, large surface area, high adsorption capacity, acidity and form selectivity [5,6]. There are two types of zeolites which are often used as adsorbents namely synthetic zeolites and natural zeolites.

Some researchers have reported the results of ammonia processing using adsorption methods using zeolites. According to Xue *et al.* [7], modernite zeolites were the most effective ammonia adsorbent compared to Bear river zeolite, modified Bear river zeolite and Y zeolite. Nuernberg *et al.* [8] used zeolite basalt and Cuban zeolite as adsorbents to reduce ammonia emissions from poultry droppings. Zeolites can be used to remove ammonia on waste treatment process [9] and landfill leachate [10]. Another study conducted by Markou *et al.* [11] proved that the amount of ammonia that can be absorbed by zeolite is 6.89 ± 0.64 mgN g^{-1} for synthetic waste and 8.89 ± 1.84 mgN g^{-1} zeolite for real waste.

Indonesia is one of the countries that is rich in natural zeolites and it widespreads in various locations, such as Malang, Sukabumi, Lampung, Bayah, Tasikmalaya and South Sulawesi. Although its structure contains many impurities, natural zeolites have good activity after being activated and modified. Its abundance and relatively cheap price make it possible to use natural zeolites as an adsorbent.

Zeolite adsorption capacity can be increased by changing its characteristics using several methods such as ion exchange with alkaline, acidification, heat treatment and addition of aluminum [12]. According to Hernawan *et al.* [13], modification of Gunungkidul natural zeolite using HCl can increase the surface area up to 5 times greater than the unmodified natural zeolite. Other studies have shown that modification using HCl, NaOH, NaCl and NH_4NO_3 increase ion exchange capacity for heavy metals [14-17]. Niu *et al.* [18] showed that zeolite modified by ion exchange method using NH_4NO_3 and heat treatment can form H-zeolite.

In this study, the activation process and modification of Bayah and Lampung natural zeolites will be carried out physically and chemically. Physical activation is done by reducing the size, filtering and heating. Chemical modification is done by acidification and ion exchange methods using HCl and NH_4NO_3. Activation and modification are carried out to obtain H-zeolite and increase the adsorption capacity of zeolite to ammonia. The result of the process will be analyzed using X-ray fluorescence (XRF) characterization and Fourier transform infrared (FTIR) to find out changing on the composition and structure. The zeolite surface area before and after activation and modification will be analyzed using the BET method.

EXPERIMENTAL

This study used zeolites from Indonesia, precisely Lampung and Bayah. Chemicals used for activation and modification of zeolites were demin water, HCl 6 M (Merck) and NH_4NO_3 1 M (Merck). Chemicals for the zeolite performance test were used 25 % NH_4OH solution (Merck).

Natural zeolite preparation: Natural zeolite weas prepared with several physical and chemical stages. Natural zeolite present in granular form was crushed and sieved to obtain particle size of 2-5 mm. After sieving, zeolite was washed using demineralized water to remove impurities attached to the zeolites. Then the zeolite was filtered to separate impurities that was carried by water. The filtered zeolite was dried out using an oven at 120 °C for 3 h. After drying, the zeolite was placed into two containers weighing 50 g each. The zeolite in the first container was soaked in 200 mL of 6 M hydrochloric acid solution, by heating at 80 °C and stirring for 3 h. Then the zeolite in another container was soaked in 200 mL of 1 M ammonium nitrate solution for 24 h with stirring and heating for 3 h at 80 °C. Zeolite which has been soaked with hydrochloric acid or ammonium nitrate was washed using demineralized water. After washing, the zeolite was dried out to evaporate the water that was still attached to the zeolite. Drying was carried out at 120 °C for 3 h. The last step was the calcination process. This process was carried out to open zeolite pores, evaporate the crystalline water contained in the zeolite structure and increase thermal stability. Calcination was carried out at 500 °C for 4 h.

Characterization: Chemical composition of natural zeolite before and after modification were analyzed using X-ray fluorescence (XRF) ICEL 2800 type spectrometer M04. The XRF characterization was also carried out to determine the Si/Al zeolite ratio. Group formed from the Brønsted Lewis acid site was observed using the Fourier transform infrared, Thermo Scientific FTIR type Diamond Nicolet IS 5 at a wave rate of 500-4000 cm^{-1} with a resolution of 32 cm^{-1} and the number of scans 64 times. Calculation of zeolite surface area before and after modification were analyzed using the BET method. This characterization uses the Autosorb iQ quantachrome brand with nitrogen as a gas analyzer.

Performance test of modified zeolites: 20 g modified zeolites were added to 500 mL amonia solution (50 ppm) in a beaker glass. Then a mixture of ammonia solution and zeolites were stirred using a magnetic stirrer. Sample was taken every 30 min for 3 h to find out the concentration of ammonia at reactor output. The ammonia residue contained in the solution was analyzed by the Nessler method using a UV-visible spectrophotometer. The measurement of concentration was carried out three times for each sample and the final value of concentration was averaged.

RESULTS AND DISCUSSION

XRF and BET of natural zeolites before and after modification: The zeolite activation and modification process aims to obtain H-zeolite and increase the adsorption capacity of Lampung and Bayah natural zeolites. Some terms used to simplify description in the pictures and tables of results. The terms are: Lampung natural zeolite (LNZ), Bayah natural zeolite (BNZ), Lampung natural zeolite HCl (LNZH), Lampung natural zeolite ammonium nitrate (LNZA), Bayah natural zeolite HCl (BNZH) and Bayah natural zeolite ammonium nitrate (BNZA).

The increase in adsorption capacity can be observed from changes in chemical composition and Si/Al ratio. XRF characterization results can be seen in Table-1. Table-1 shows that there is a change in chemical composition and an increase in the Si/Al ratio in zeolites after modification. This increase in Si/Al ratio is caused by the dealumination process resulting in the removal of Al from the zeolite framework due to acid treatment [19-21]. The Si/Al ratio increased more significantly in LNZH and BNZH because immersion in 6 M HCl which is a strong acid was able to dissolve aluminum oxide from the inner framework in the crystal into the outer framework and push it out of the zeolite structure. In LNZA and BNZA, the increase in Si/Al ratio is not too much. This is because ammonium nitrate only push aluminium oxide which is outside crystal frame exit the zeolite structure. The Si/Al ratio is one of the parameters that determine the nature of zeolites. Zeolites with a high Si/Al ratio have significant adsorption and ion exchange capability [22,23].

Another parameter to determine the nature of zeolite is surface area. The aims of modifying natural zeolites is to increase its surface area. The BET characterization results in Table-2 prove that the modified zeolite has a larger surface area. The increase in zeolite surface area is due to the dealumination process and removal of impurities that cover the pore so that

TABLE-1
NATURAL AND MODIFIED ZEOLITES CHEMICAL COMPOSITION

Element	LNZ	LNZH	LNZA	BNZ	BNZH	BNZA
Silica	79.91 %	78.20 %	76.90 %	64.56 %	78.20 %	74.70 %
Aluminium	11.67 %	7.80 %	10.9 %	10.62 %	8.50 %	10.70 %
Ratio Si/Al	6.85	10.03	7.06	6.08	9.20	6.98

LNZ = Lampung natural zeolite, LNZH = Lampung natural zeolite HCl, LNZA = Lampung natural zeolite ammonium nitrate, BNZ = Bayah natural zeolite, BNZH = Bayah natural zeolite HCl, BNZA = Bayah natural zeolite ammonium nitrate

TABLE-2
NATURAL AND MODIFIED ZEOLITES SURFACE AREA

Sample	BET surface area (m^2/g)
LNZ	49.854
LNZH	102.337
LNZA	64.421
BNZ	47.450
BNZH	86.236
BNZA	51.525

the zeolite pores become exposed and the surface is wider [21]. Increased surface area in line with increasing Si/Al ratio [20]. Increased surface area is also due to the calcination process. Calcination causes the evaporation of water molecules from inside the crystal to form a cavity with a larger surface [24]. This increase in surface area can also be seen in the N_2 adsorption isotherm curve as shown in Fig. 1. In the figure it can be seen that the volume of N_2 adsorbed by LNZH and BNZH is greater than that of other zeolites. LNZH and BNZH get the most significant increase in surface area of 102.337 m^2/g and 86.236 m^2/g compared to the unmodified zeolite which was 49.854 m^2/g for LNZ and 47.450 m^2/g for BNZ. Modified zeolites by acid treatment have a larger surface area than zeolite modified by cation exchange. This characterization results are in accordance with the research conducted by Liu *et al.* [25] which proved that modification of zeolite with acid treatment produced the largest surface area.

FTIR characterization: Dealumnination process can increase the number of acidic sites on the surface of zeolite [21]. Likewise the cation exchange process of K, Fe and Ca with NH_4^+ can increase the total acidity of zeolite [14]. The zeolite immersion process into NH_4NO_3 causes an exchange of cations between alkaline cations in zeolites with NH_4^+ cations [26]. When the calcination process occurs NH_4^+ cations was decomposed into H^+ ions so that forms H-zeolite [27]. Cation exchange mechanism can be seen in Fig. 2.

The presence of H^+ ions in the zeolite framework can form hydroxyl groups [14]. Changes in the Brønsted acidity level

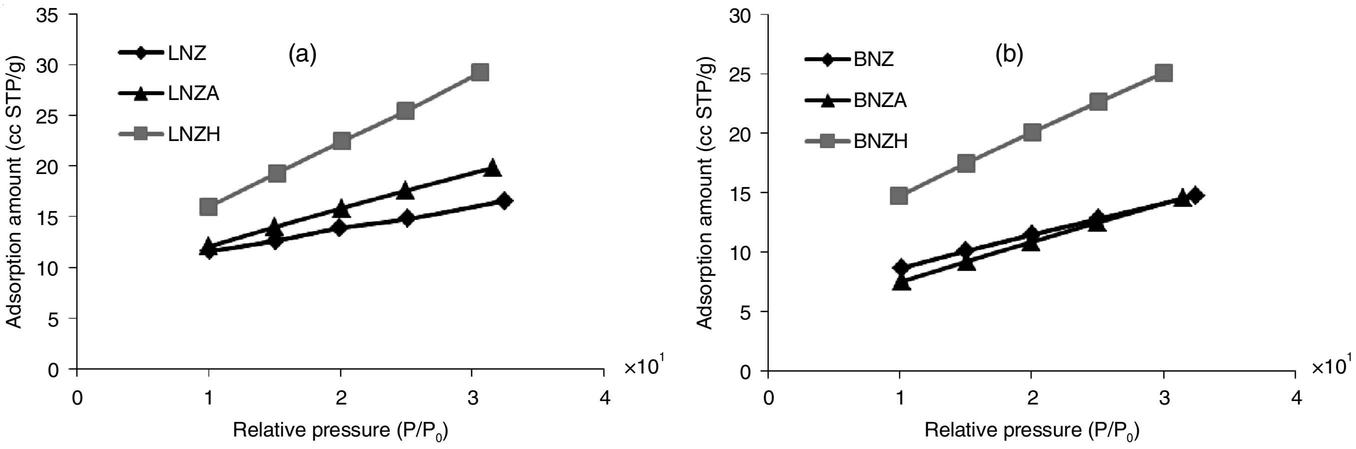

Fig. 1. Nitrogen adsorption isotherms of zeolite (a) Lampung natural and modified zeolit, (b) Bayah natural and modified zeolite at 77 K

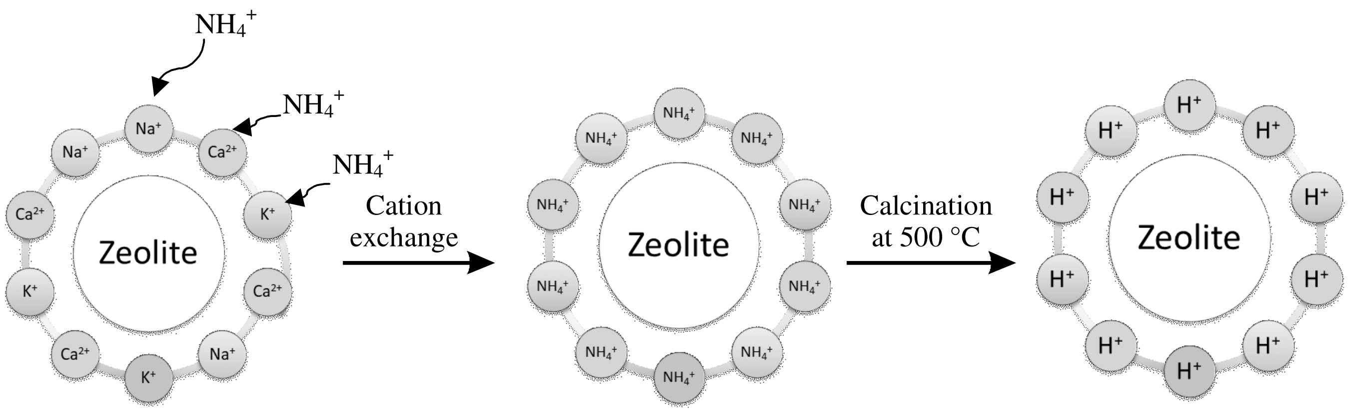

Fig. 2. Mechanism of cation exchange in zeolites when it immersed into NH_4NO_3 solutions and calcination process

can be observed by the presence of OH groups at wavenumbers 3610 cm^{-1} and pyrH$^+$ in the wave number 1545 cm^{-1}. OH groups mainly located in non-framework aluminum species can be observed at 3660 cm^{-1}. The formation of Lewis-acidic sites observed with an increase in coordinatively coordinated pyridina absorption bands appeared in 1590-1625 and 1454 cm^{-1}. Peak at 3728 cm^{-1} for the silanol group in zeolite crystals. Peak width at 3500 cm^{-1} is observed for the Si-OH group in the hydroxyl group, which is thought to originate from the delocalised hydrogen bond [18].

Natural zeolite and modified zeolite FTIR spectra were observed in the range of wavenumber 4000-500 cm^{-1}. Fig. 3 shows that there are OH and pyrH$^+$ groups at wavenumbers of 3640 cm^{-1} and 1623 cm^{-1}, respectively. The detected OH group is predicted to be located around non-aluminum species. This shows the formation of the Brønsted acid site. The pyrH$^+$ group shows the formation of the Lewis acid site.

Table-3 shows that there is an increase in transmittance intensity on activated zeolites. Brønsted and Lewis acid sites in natural zeolites which have been activated was change due to the exchange of alkaline ions with H$^+$ ions. Increasing OH and pyrH$^+$ groups also shows that activated zeolites have more H$^+$ ions. The Bayah natural zeolite shows greater intensity changes than Lampung's. This proves that Bayah's natural zeolite is more susceptible to ion exchange than Lampung's natural zeolite. This is because the value of exchange capacity Bayah's natural zeolite is greater than Lampung's natural zeolite. Cation exchange capacity value of Bayah's natural zeolite is 96.75 me 100 g^{-1} and natural zeolite Lampung 87.72 me 100 g^{-1} [28].

TABLE-3
COMPARISON TRANSMITTANCE
INTENSITY IN SPECIFIC WAVENUMBER

Sample	Intensity at 3640 cm^{-1} (au)	Intensity at 1623 cm^{-1} (au)
LNZ	96.00	95.80
LNZH	96.93	96.42
LNZA	97.50	97.90
BNZ	94.36	93.54
BNZH	97.40	97.30
BNZA	97.80	97.50

Zeolite performance as ammonia adsorbent: In this study, the performance tests of two natural zeolites were carried out before and after being modified to adsorb ammonia. The initial ammonia concentration is 50 ppm. The mechanism of ammonia adsorption on zeolite can be path in 2 ways. The first method is the exchange of ammonia ions in the form of NH_4^+ with the cations found in zeolite [29]. The second method is the binding of ammonia in the form of NH_3 to the H$^+$ ion in the modified zeolite framework.

The effect of zeolite modification on the concentration of the reactor output can be seen in Fig. 4. The adsorption process by modified zeolite showed a smaller concentration of ammonia than adsorption by unmodified natural zeolite. LNZA, LNZH, BNZA and BNZH could adsorb ammonia to below the quality standard (< 25 ppm). Modified zeolites could also remove ammonia at a higher adsorption rate. This can be seen in the 30th min, where the concentration of ammonia has reached the quality standard. Fig. 4 also shows that Bayah natural zeolite has a higher adsorption rate than Lampung natural zeolite.

Fig. 5 shows the maximum percentage of ammonia removal carried out by zeolite. It can be seen that ammonia adsorption has increased after zeolite is modified. The maximum removal of ammonia at LNZ is 53.18 % and BNZ is 45.25 %. After zeolite was modified by acid treatment (HCl immersion) and ion exchange (NH_4NO_3 immersion), the percentage of ammonia removal increased to 68.13, 62.96, 70.71 and 64.80 % for BNZH, LNZH, BNZA and LNZA.

The results of the adsorption test showed that zeolite modified by ion exchange method had a greater adsorption capacity than zeolite modified with acid treatment. This is due to modification using HCl resulting more dealumination so that the amount of Al that is bound to the frame becomes less. This small amount of Al causes the negative charge to decrease so that the alkaline cation also shifts out of the frame. The reduced number of alkali cations in the framework causes the alkali cation exchange process in zeolite with NH_4^+ ions in ammonia becomes less. This phenomenon is also caused by modification with ion exchange resulting in H-zeolite. This type of zeolite can bind NH_3 with H$^+$ ions so that it is not easily absorbed. The results of the adsorption test also proved that

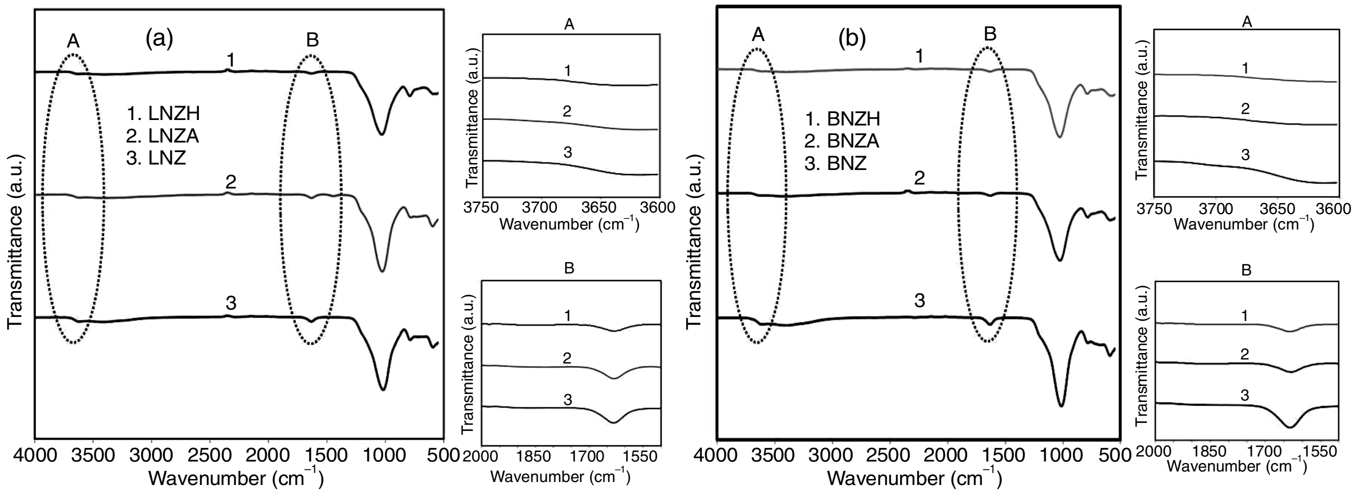

Fig. 3. FTIR spectra for zeolite (a) Lampung natural and modified zeolit, (b) Bayah natural and modified zeolite

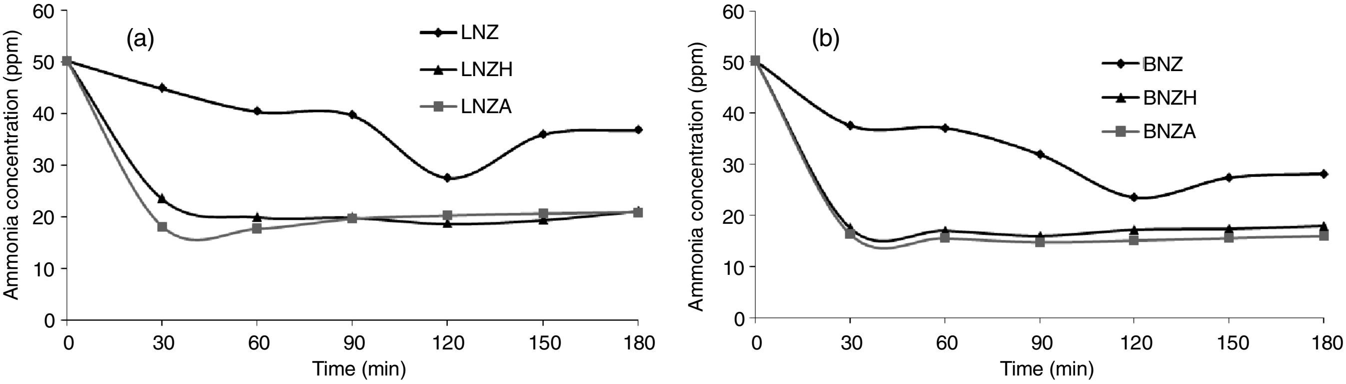

Fig. 4. Effect of zeolite modification on ammonia concentration at reactor output, operating condition: C_0 = 50 ppm, volume = 500 mL and weight of zeolite = 20 g, (a) Lampung zeolite, (b) Bayah zeolite

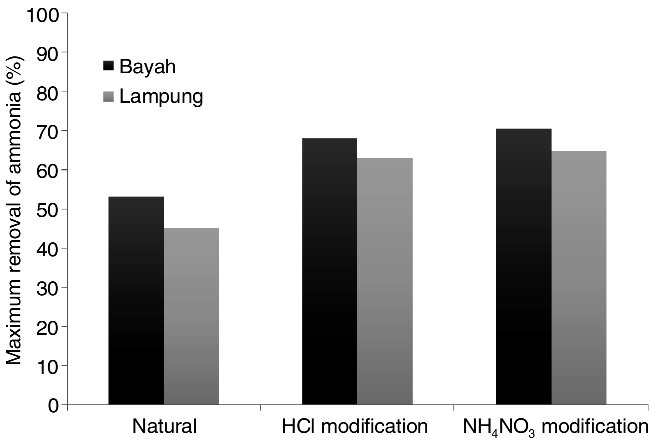

Fig. 5. Effect of zeolite modification on maximum removal of ammonia

the Bayah's natural zeolite before and after modification had a greater ammonia adsorption capacity because the Bayah's natural zeolite had a greater cation exchange capacity than Lampung's natural zeolite [28]. Zeolites wich have greater cation exchange capacity could adsorb ammonia (in NH_4^+ form) better [30].

Conclusion

After being modified with acid treatment methods, ion exchange and calcination, zeolites undergo significant structural changes. Based on the XRF characterization result, the modified Lampung's natural zeolite has a change in composition and an increase in the Si/Al ratio. The zeolite surface area increased from 49.854 m^2/g for LNZ to 102.337 and 64.421 m^2/g for LNZH and LNZA. The surface area of Bayah's natural zeolite increased from 47.450 m^2/g for BNZ to 86.236 and 51.525 m^2/g for BNZH and BNZA. Changes in the intensity of hydroxyl groups and $pyrH^+$ show that there is an increase in total acidity of zeolites due to dealumination and cation exchange. The Bayah's natural zeolite ammonia removal percentage is greater than Lampung's natural zeolite because the Bayah's natural zeolite cation exchange capacity is greater than Lampung's. Zeolite modified by ion exchange method can adsorp ammonia more than zeolite modified by acid treatment.

The results of zeolite performance test after modification showed that both methods of modification were successfully conducted on Lampung and Bayah natural zeolite. It might be both of methods can be used for all types of zeolite. The modification method of natural zeolite to enhance the effectiveness of ammonia adsorption can still be continued by combining the two methods (acid treatment and cation exchange).

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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