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Low Temperature Thermal Activation of Sarulla Natural Zeolite for Ammonia Removal Using Fixed Bed Column Adsorption Process

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ABSTRACT

A local natural zeolite from Sarulla in North Sumatra has been isolated and activated with low thermal activation process to enhance its ammonia adsorption capacity. The Sarulla Natural Zeolite (SNZ) was prepared through crushing, sieving, washing, and thermal activation at 120 °C for three hours. SNZ was further characterized and tested for ammonia removal using batch and fixed bed column adsorption processes. In the fixed bed column adsorption, the bed height and initial ammonia concentration were used to understand the adsorption process. The batch adsorption result demonstrates the low thermal activation process improves approximately 10% of the adsorption capacity of SNZ. The kinetics study confirmed that the ammonia adsorption mechanism is chemisorption mechanism where the initial concentration plays the role in determining the mass transfer driving force. Furthermore, the rise on bed height do not provide more contact sites and extend the breakthrough time due to lack of flow blockage. The flow blockage limits the contact between zeolite and ammonia which further perform low adsorption capacity. 2 cm of bed height with 150 mg/L of initial concentration exhibit the highest adsorption capacity of 15.3551 mg/g. The result shows that the low thermal activation approach is an effective way to improve the SNZ adsorption capacity.

Keywords: Sarulla natural zeolite, low thermal, ammonia removal, fixed bed column.

INTRODUCTION

As one of the world's largest shrimp exporting countries since 1987, Indonesia has become important suppliers of shrimp to the market in Japan, European Union and United States. Currently, Indonesia is reported as the third largest shrimp producers after China and Thailand [Wati, 2018]. Approximately 90% of the shrimp production is obtained from cultivation farms where most of the imported shrimp (95%) is exported and 5% of the production is used for domestic market demands [Wati, 2018; Statista, 2024]. The intensive shrimp cultivation could be followed by ensuring the high quality cultivated product to maintain the sustainable production. However, the most common problem on the shrimp cultivation is the presence of high ammonia concentration on the water body as a byproduct of undigested feed, feces and shrimp metabolites [Tong et al., 2023]. The ammonia concentration on the water body determines the shrimp development, shrimp quality product, and the successful of cultivation process [Anggoro et al., 2023]. For example, the high ammonia concentration could affect the water ecosystem by stimulating nuisance algae growth in polluted waters and reduced surface water quality [Huang et al., 2017]. Therefore, the ammonia concentration on the shrimp cultivation and farm water bodies should be controlled periodically and removed using an effective and low cost processes.

The presence of ammonia from water can be eliminated using several treatments such as biological treatment, physical treatment, chemical treatment, and combination between two processes [Zhu et al., 2024]. Biological treatment is the most explored and mature technology where chemical and physical treatment are still under research and development. However, the physical treatment could potentially support the ammonia removal and recovery [Zhu et al., 2024]. The adsorption is the most researched technology on physical treatment where adsorbents could adsorb the ammonia and recovery the ammonia after treatment [Han et al., 2021]. To be specific about adsorbent, natural zeolite is reported as the most used adsorbent to treat water on the shrimp cultivation pond in Indonesia because of its abundant material and relatively cheap [Anggoro et al., 2023]. Natural zeolite is defined as a zeolite formed naturally by environment changes with three dimensional frameworks of aluminium tetraoxide ($[AlO_4]^{-5}$) and silicon tetraoxide ($[SiO_4]^{-4}$) that are connected by oxygen atoms. The zeolite frameworks form the negative charge of natural zeolite that further utilized to adsorb the positive charge cations like ammonia [Sintya, 2021]. Several previous research about the adsorption process for ammonia removal have been reported [Alshameri et al., 2014b; Alshameri et al., 2014a]. However, natural zeolite relatively has low adsorption capacity that depends on clay-type content and their physicochemical properties. Thus, the farmers should purchase the zeolite in high quantity to treat the shrimp cultivation water. Modification and treatment of natural zeolite could be made through acid, base, salt treatment, cationic sufactan modification, or metallic functionalization [Kuldeyev et al., 2023]. Speaking to technical feasible for shrimp cultivation, the chemical activation is not possible implemented due to lack of access and high cost of treatment. The low cost treatment with high improvement should be done to support the shrimp farmer, especially traditional farmer in Indonesia.

The present study aims to apply low thermal activation process to improve the adsorption capacity of natural zeolite from Sarulla sub-district known as SNZ. The low thermal activation aims to provide a low cost treatment which could be implemented in Indonesia. To characterize the zeolite performance, a combination of batch and continuous fixed bed column adsorption processes is employed where the synthetic ammonia solution was used for the adsorbate media. To be more specific on fixed bed colum adsorption, the effect of bed height and ammonia initial concentration on ammonia are used. The data obtained from the experiment are further analysed using Thomas and Yoon-Nelson kinetic models to study adsorption rate constant, ammonia adsorption capacity

and time required to reach 50% of the adsorbent breakthrough. The result is expected to show the performance of SNZ before and after low thermal temperature process, the percentage of adsorption improvement and the adsorption mechanism. The result will give a better understanding for the local government to utilize the SNZ and provide a better additional value by activating the SNZ using low cost treatment process.

METHODS

Preparation of Sarulla natural zeolite using low temperature thermal activation process

The SNZ was obtained from Sarulla subdistrict at Pahae Jae district in North Tapanuli regency, North Sumatra Province, Indonesia. The detailed coordinate is located on on 1°45'15" N and 99°08'24 E. SNZ is well known locally as the zeolite used for treating the water on the shrimp farming pond. To prepare and treat the SNZ, the chunks of SNZ was crushed and sifted using 100 mesh sieves followed by washing process with distilled water where the precipitated powder was taken for further treatment. The obtained powder was rewashed with destilled water for several times until the white clear solution achieved. The clean SNZ was heated at 105 °C for 1 hour and assigned as non-treated SNZ (SNZ-C). To enhance the adsorption process, the SNZ was heated at 120 °C for three hours with the heating rate of 10 °C and signed as SNZ-T. Furthermore, the obtained samples were characterized using Fourier Transform Infrared (FTIR, Shimadzu, IRPresige 21) to confirm the zeolite material based on its functional group.

Ammonia removal experiment to assess the adsorption properties of SNZ

Combination of batch and fixed bed column experiments were conducted to investigate the ammonia removal performance of SNZ-C and SNZ-T. To compare the adsorption capacity, a rasio 1:10 (w/v) between SNZ and 100 mg/L of ammonia solution was designed for batch adsorption process with 300 rpm of continuous stir for 180 minutes. To be more specific in investigating the performance of SNZ-T, the fix bed column experiment with 2 cm of glass column with with 100 cm height at room temperature was used. The column was filled with adsorbate between cotton to compact the adsorbate and prevent the adsorbate loss due to liquid flows. To avoid the air bubbles and high pressure on the liquid flow, the column was filled with 6 mm and 2 mm glass beads in the bottom of column and 2 mm glass beads in the top of column. Figure 1 shows the proposed fixed bed column adsorption process.

To conduct the adsorption test, approximately 500 mL synthetic ammonia solution was used to see the SNZ-T adsorption properties with a controlled flow rate at 25 mL/min. Three levels of bed height of SNZ-T was used to investigate the effect of bed height on the ammonia adsorption process. At the same time, the initial concentration of ammonia solution was varied into three levels which were 100 mg/L, 125 mg/L and 150 mg/L. Each process of experiment was set a at pH 7 by carefully adding 0.1 M H_2SO_4 . The continuous adsorption process was run for 180 minutes to provide a maximum contact time between zeolite and ammonia with 10 minutes of sampling interval.

To control the adsorption removal, 5 mL of ammonia solution sample was taken during the adsorption experiment (batch and fix bed column processes) and its concentation was controlled using UV-Vis Spectrophotometer (Cary 60 Agilent Technologies) with Fenat Method according to Indonesian Standard for Ammonia Testing Method abbreviated as Standard Nasional Indonesia with Testing Number of 06-6989.30-2005.

Ammonia removal on batch adsorption process

The number of adsorbed ammonia in the batch adsorption experiments is evaluated by calculating the adsorption capacity using the following Equation 1.

$$Q = \frac{(C_0 - C_t) \times V}{m} \tag{1}$$

where: C_0 and C_t (mg/L) are the concentration of ammonia at the beginning and after a certain contact time, respectively. V (liter) is the volume of solution and m (gram) is the amount of adsorbent [Anh et al., 2024].

To investigate the adsorption mechanism, the obtained results of batch adsorption are utilized by the pseudo first and second orders. The pseudo first and second kinetics model are also used to calculate the rate of adsorption process using the following Equation 2 and 3, respectively.

$$\operatorname{Ln}(Q_e - Q_t) = \operatorname{Ln}Q_e - k_I \cdot t \tag{2}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 \cdot Q_e^2} + \frac{t}{Q_e} \tag{3}$$

where: Q_e is the adsorption capacity at the equilibrium phase (mg/g), Q_t is the adsorption capacity at time t (mg/g), k_1 is the first order adsorption rate constant (min⁻¹), k_2 is the second order adsorption rate constant (min⁻¹), and t is the contact time (min).

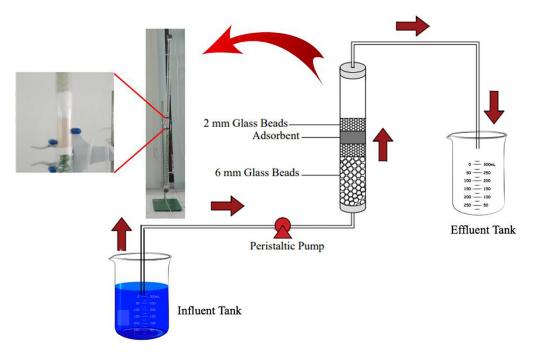


Figure 1. Proposed fixed-bed column adsorption design for ammonia removal

Adsorption kinetic models for fixed bed column adsorption

The number of adsorbed ammonia in the fixed bed column adsorption experiments is evaluated using the experimental breatkthrough curves [Attia et al., 2018]. Thomas and Yoon-Nelson models are the mathematical models used to describe the SNZ-T performance in the fixed-bed column adsorption obtained from the experimental data. The linear equations of Thomas and Yoon-Nelson model are shown in Equation 4 and 5, respectively.

$$Ln\left[\frac{c_0}{c_t} - 1\right] = \frac{\kappa_{TH}q_0^m}{Q} - K_{TH} \cdot Co \cdot t \qquad (4)$$

$$Ln\left[\left(\frac{Ct}{Co-Ct}\right)\right] = K_{YN} \cdot t - K_{YN} \cdot \tau \qquad (5)$$

where: C_t is ammonia concentration at time t (mg/L), C_0 is ammonia initial concentration (mg/L), t is contact time (min), Q is influent flow rate (mL/min), m is the mass of adsorbent (g), K_{TH} is Thomas adsorption rate constant (L/min.mg), K_{YN} is Yoon-Nelson adsorption rate constant (min⁻¹) and τ is time required to reach 50% of the adsorbent breakthrough (min) and q_0 is adsorption capacity of adsorbent (mg/g).

Thomas and Yoon-Nelson Models have different purposes on the adsorption modelling in the fixed bed column. Thomas models aims to prove that the surface reaction between SNZ and ammonia conducted in the surface of SNZ. It means that the adsorption process is only affected by the unused capacity of SNZ and ammonia. On the other hand, the Yoon-Nelson model aims to provide an understanding that adsorption process is equilibrium between adsorbate adsorption and adsorbate breakthrough on the SNZ [Radhika et al., 2018].

RESULT AND DISCUSSION

Low temperature thermal activation aims to provide a suitable approach to enhance the SNZ adsorption properties using a low cost and minimum treatment infrastructure. The use of low temperature thermal activation also possesses green technology without adding any preservative to boost the adsorption capacities. This approach is important since most of SNZ having low adsorption capacity and most the activation method using chemical which sometimes do not provide a significant booster rather than producing byproduct which could form a toxic component [Anggoro et al., 2021]. The use of chemical activation using base solution decreases the adsorption performance of SNZ due to form of silanol bond and rough/lump surface [Gea et al., 2020]. On the other hand, the facile and feasible technique such as low thermal activation method is suitable to develop in the original area of SNZ in Pahae Jae district in North Tapanuli regency, North Sumatera Province, Indonesia. In the present study, fourier transform infra red (FTIR) analysis have confirmed the natural zeolite framework band of $[SiO_4]^{-4}$ and $[AlO_4]^{-5}$ obtained at 997.2 cm⁻¹ and 1107.04 cm⁻¹. The supporting band spectrum at wavenumbers of 1644.71 cm⁻¹, 2391.73 cm⁻¹ and

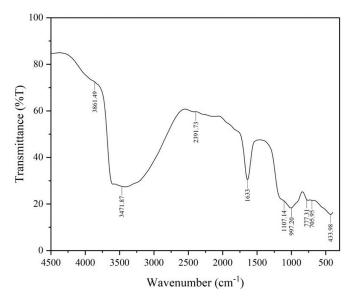


Figure 2. FTIR data of SNZ after low thermal temperature treatment

3471.87 cm⁻¹ are attribute to hydroxyl (OH) functional group (Figure 2). The result of SNZ bands are correlated to the reports of other Indonesian NSZ found on the other places such as Lampung [Elysabeth et al., 2019], Tasikmalaya [Dewi et al., 2017], Ende - Nusa Tenggara Timur [Noelaka et al., 2018], etc. This result confirm that the structure of NSZ found in Indonesia is relatively similar in the functional groups perspective. To test the initial adsorption performance of SNZ-C and SNZ-T, the conventional batch adsorption process have conducted. In general, Figure 3a told a higher adsorption capacity of SNZ-T compared to SNZ-C. There is approximately 10% of adsorption capacity boosting after treating the SNZ-C with low temperature thermal activation. Based on the potential framework of SNZ in Indonesia, the main possible reason of adsorption capacity improvement is because of the hydration process which provide a large adsorption capacity for ammonia where there is no modification involved in the low temperature thermal activation [Bish et al., 2001]. Furthermore, the kinetics analysis support the adsorption capacity enhancement where the thermal activation could boost the adsorption capacity of SNZ-C. Based on the kinetics model, the adsorption capacity

of SNZ-C enhance approximatel 7% and 24% based on the pseudo first order and pseudo second order, respectively. The detail of adsorption capacity improvement were shown in additional table on Figure 3b and 3c. Furthermore, the mechanism of adsorption process tend to fit with the pseudo second order model based on the coefficient of determination (R²). The result proved that the interaction between the functional group of SNZ and ammonia ions is more ical affinity or chemisorption mechanism [Liu et al., 2022].

The adsorption test was continued by fixed bed column adsorption technique using SNZ-T as the adsorbent. Variations of adsorbent bed height used in this experiment which are 2 cm, 4 cm and 6 cm which equals in weight to 4 gram, 8 gram and 12 gram of SNZ-T, respectively. Figure 4 shows the effect of bed height on the ammonia removal is shown in Figure 4 as the breakthrough curve of ammonia removal. Figure 4a showed that the narrow bed height of 2 cm performs the fastest and highest ammonia removal performance as a function of adsorbent bed height. The C/C_{a} values for bed height 2 cm, 4 cm and 6 cm at 180 minutes sequentially are 0.810; 0.763 and 0.693, respectively. Increasing the bed height could provide longer breakthrough time since the ammonia

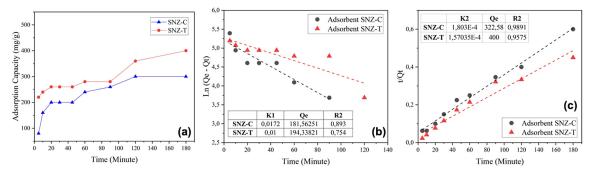


Figure 3. Ammonia removal of SNZ-C and SNZ-T in batch adsorption: (a) adsorption capacity; (b) pseudo first order; and (c) pseudo second order

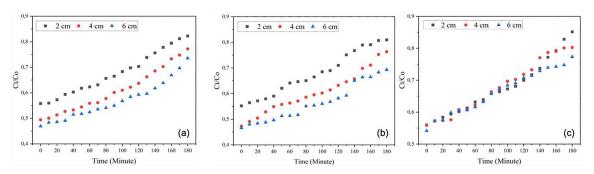


Figure 4. Breakthrough curve at different adsorbent bed height with ammonia initial concentration (a) 100 mg/L, (b) 125 mg/L and (c) 150 mg/L

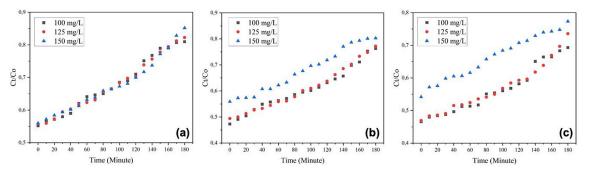


Figure 5. Breakthrough curve at different ammonia initial concentration with adsorbent bed height (a) 2 cm, (b) 4 cm and (c) 6 cm

should contact with more SNZ-T surface site. However, the present study found that the low performance of higher bed height of SNZ is initiated by the limited binding site of SNZ-T due to the pollutant blockage flowing from the bottom to top. On the other hand, the saturated layer in the bottow of bed initiates the blockage of ammonia solution penetration which deflects the flow pattern to the edge of column which form low adsorption performance. Similar results are also shown at Figure 5b and 5c where the C/C_{o} values decrease with increases of adsorbent bed height for each ammonia initial concentration variation. The smaller C_t/C_a values means the higher ammonia removal values because of the increases of adsorbent bed height. When the amount of adsorbent used in the adsorption process increases, the binding site for adsorbate also increases and leads to higher ammonia removal [Omitola et al., 2022]. Increasing the adsorbent bed height also leads to a longer time to reach saturation point [Selambakkannu et al., 2019]. The C/C_{a} values from the adsorption process with all variations of bed height is below 1 and this shows the adsorption process still has not reached the saturation point. The saturation point of the continuous adsorption process occurs when the adsorbent is saturated with ammonia and could not adsorb the ammonia molecule from the adsorbate. When the adsorbent reaches the saturated point, the C/C_o value in the breakthrough curve is 1.

The effect of ammonia initial concentration used in the experiments on the ammonia removal is shown in Figure 4. The result proved that the value of C_l/C_o is differentiated by the bed height of adsorbate. 2 cm bed height showed the highest value of C_l/C_o in any concentration with the highest C_l/C_o is coming from the largest concentration of ammonia concentration. Higher ammonia initial concentration also causes the saturation time of the adsorbent to occur faster compared to lower ammonia initial concentration [Cundari et al., 2020]. However, all condition showed the values of Ct/Co under 1 which mean the adsorbate is not in the saturated points.

The kinetics analysis support the breakthrough result shown at Figure 5 and 6. In general, the correlation coefficient from plotted data is above 0,9 and this means Thomas and Yoon-Nelson models are suitable to describe the performance of fixed bed column adsorption experiments (Table 1). To be more specific, the increasing of initial concentration exhibits minor change on K_{TH} and increase q_0 of proposed models. The rise in the K_{TH} on

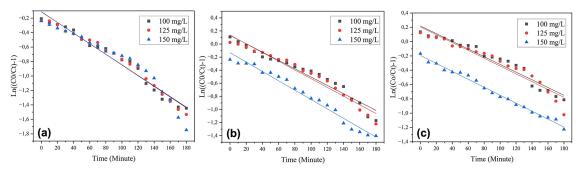


Figure 6. Fixed bed column adsorption experimental data using Thomas kinetic plot at different ammonia initial concentration with adsorbent bed height (a) 2 cm, (b) 4 cm and (c) 6 cm

		Thomas model			
Adsorbent bed height (cm)	Ammonia initial concentration, <i>Co</i> (mg/L)	Thomas adsorption rate constant, $K_{_{TH}}$ (mL/min.mg)	Maximum adsorption capacity, q_o (mg/g)	R ²	
2	100	0.0000730	14.0319	0.9732	
	125	0.0000584	14.8040	0.9686	
	150	0.0000493	15.3551	0.9149	
4	100	0.0000640	3.8793	0.9519	
	125	0.0000536	3.9845	0.9583	
	150	0.0000480	4.0240	0.9765	
6	100	0.0000540	2.6136	0.9469	
	125	0.0000440	2.6443	0.9246	
	150	0.0000373	2.6669	0.9906	
		Yoon-Nelson model			
Adsorbent bed height (cm)	Ammonia initial concentration, <i>Co</i> (mg/L)	Yoon-Nelson adsorption rate constant, <i>K</i> _{YN} (min ⁻¹)	Time to reach 50% of breakthrough, (minute)	R ²	
2	100	0.0073	15.5068	0.9732	
	125	0.0073	15.3699	0.9686	
	150	0.0074	14.8243	0.9149	
4	100	0.0064	20.5156	0.9519	
	125	0.0067	20.3284	0.9583	
	150	0.0072	18.3333	0.976	
6	100	0.0054	40.6296	0.9469	
	125	0.0055	37.4000	0.924	
	150	0.0056	34.5179	0.990	

Table 1. Parameter values of Thomas and Yoon-Nelson models

the lower initial concentration indicates the high mass transfer driving force on the lower concentration of ammonia which means the more adsorbate have contacted to the active surface of SNZ-T [Tran et al., 2024]. Furthermore, the increase of q_0 value on higher initial concentration provides a more occupied surface of SNZ-T, leading to more adsorption capacities. However, the higher bed height do not support more adsorption sites to adsorb the ammonia due to the lack of dynamic

flow pattern [Selambakkannu et al., 2019]. The experiment result show that the initial concentration affect the ammonia adsorption through enhancing the mass transfer driving force in low initial concentration, also referred to as the concentration gradient from the solution to the SNZ-T surfaces, intensifies [Tran et al., 2024]. The slope from the plotted data in Figures 6, 7 represents the Yoon-Nelson adsorption rate constant (min⁻¹) and the intercept represents the time required

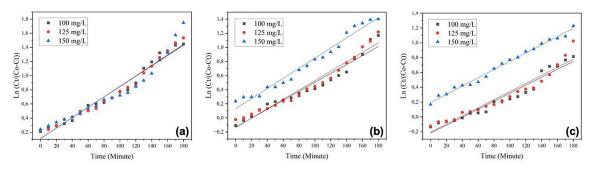


Figure 7. Fixed bed column adsorption experimental data using Yoon-Nelson kinetic plot at different ammonia initial concentration with adsorbent bed height (a) 2 cm, (b) 4 cm and (c) 6 cm

Journal of Ecological Engineering 2024, 25(11), 354-364

for the effluent concentration to reach 50% of the adsorbent breakthrough (minute). From the Equation 4, the value of graphical slope values indicates the value of the Yoon-Nelson adsorption rate constant which also means the time required for the effluent concentration to reach 50% of the adsorbent breakthrough. The rise on K_{VN} value on the higher initial concentration shorten the time to reach 50% of the adsorbent breakthrough (τ) which indicates the contact period between adsorbent and adsorbate occurs faster and decrease the efficiency of ammonia adsorption on the surface of SNZ-T. This pattern is also occurred in the other bed height. Furthermore, the increase of bed height relatively showed minor K_{TH} change which means the increase of bed height do not change the adsorption rate of ammonia. For example, the amount of SNZ-T used in the experiment is increased by twice by adding 4 cm of bed height from 2 cm, the ammonia removal only increases less than 8%. However, the time to reach the breakthrough show a massive change when the adsorbent bed height is 6 cm indicating the binding site of adsorbent increases and has a longer time to reach 50% breakthrough point compared to when the adsorbent bed height is 2 cm. The most optimum results is shown at bed height 2 cm and ammonia initial concentration 150 mg/L with maximum ammonia adsorption capacity of SNZ-T is 15.3551 mg/g and time required to reach 50% of breakthrough is 14.8243 minute.

As the conclusion, the result on the fixed bed column adsorption shows better performance at bed height 2 cm compared to performance at bed height 4 cm and 6 cm where adding additional amount of SNZ-T do not significanly increase the yield of ammonia removal (< 8%). This is due to the presence of vacant space when the adsorbent bed height is too big and dense. Vacant space can be defined as a part of adsorbent bed height that is not occupied by ammonia molecules because the part is too restrictive and often occurs when using a single-layered bed [Sadon et al., 2014]. When using a single-layered bed in fixed bed column adsorption, the pressure inside the column is often too high when the flow rate of influent is high and the adsorbent bed is too thick. with high pressure and thick adsorbent bed, the adsorbate flow becomes non uniform, causing vacant space and reducing the efficiency of adsorption process. The pressure inside the column can be reduced with a multi-layered bed. Multi-layered bed can be done by separating a thick adsorbent bed to a thin layer. With lower pressure, uniform flow and high contact time between adsorbates with every active site of adsorbent, the efficiency of fixed bed column adsorption process could increase. The utilization of SNZ that has been used for ammonia removal from wastewater also needs to be conducted in the future to extend the usage period of natural zeolite material like using them as a slow-release fertilizer [Huang et al., 2017]. With more research about the valorization of ammonia-saturated natural zeolite could produce an economically valuable product and the disposal of the material could be done without causing environmental pollution.

Future direction

The adsorbent used in this study is SNZ obtained from the local farmer in the Sarulla subdistrict in Indonesia. High impurities and water contents are usually found in natural zeolite pores and were the cause of low adsorption capacity of natural zeolite. The present study have found that the low temperature thermal activation process could boost the adsorbent performance and reduce the amount of SNZ used to reduce the ammonia in the water. The technoeconomic analysis

Table 2. Estimated cost for thermal and chemical activation of sarulla natural zeolite

Low temperature thermal activation estimated cost							
Materials	Quantities	Cost	Total cost/kg SNZ (IDR)	Total cost/kg SNZ (USD) [*]			
Electricity for 4.5 kW furnace with 2 kg capacity	3 hours	Rp1.200/kWh	8.100	0.51			
Chemical activation estimated cost							
Materials	Quantities	Cost	Total cost/kg SNZ (IDR)	Total cost/kg SNZ (USD)⁺			
2 M HCI Solution	2.000 mL/kg	Rp24.000/L					
Distilled water	10.000 mL/kg	Rp2000/L	70.400	4.42			
Electricity for 4.5 kW furnace with 2 kg capacity	4 hours	Rp1.200/kWh					

Note: *1 USD = IDR 15.940.

tries to calculate the estimate cost for thermal activation of SNZ and compared it to the chemical activation process. From Table 2, the thermal activation process only needs extra cost for the electricity to dry the SNZ for 3 hours. Our previous chemical activation [Husin et al., 2024] used the combination of chemical and thermochemical process which requires a higher cost for the chemical solution, distilled water for the rinsing process and longer time to dry the SNZ [Husin et al., 2024]. The high cost of chemical or thermochemical activation is not a feasible technology for the farmers in Indonesia since it will add more production cost. On the other hand, the chemical activation process do not provide higher adsorption capacity since the failure to determine a proper concentration could initiate the change on SNZ framework [Gea et al., 2020].

CONCLUSION

Low temperature thermal activation of Sarulla Natural Zeolite have demonstrated approximately 10% of adsorption capacity improvement of SNZ. The fixed bed column adsorption process also confirm that the narrow bed height perform approximately 24% of capacity rise confirmed by the pseudo second order model. This findings opens an overview of future design reactor or chamber to treat the water or wastewater in shrimp farming area with a narrow or thin layer of SNZ to provide a faster and efficient ammonia removal. Furthermore, the initial ammonia concentration only affect minor changes on adsorption process by determine the mass transfer driving force especially on lower initial concentration. The result found that the low temperature thermal activation technique is the suitable process applied in Indonesia since it needs a simple equipment, relatively cheap, and provide an excellent improvement. This finding could be a valuable information for the local farmer and government to support the utilization of Indonesian based Natural Resource based on the ability to conduct the process.

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REFERENCES

- Alshameri, A., Yan, C., Al-Ani, Y., Dawood, A.S., Ibrahim, A., Zhou, C., Wang, H., 2014a. An Investigation into the adsorption removal of ammonium by salt activated Chinese (Hulaodu) natural zeolite: Kinetics, isotherms, and thermodynamics. Journal of the Taiwan Institute of Chemical Engineers. 2(2), 554–564. https://doi.org/10.1016/j. jtice.2013.05.008
- Alshameri, A., Ibrahim, A., Assabri, A.M., Lei, X., Wang, H., Yan, C., 2014b. the investigation into the ammonium removal performance of yemeni natural zeolite: Modification, ion exchange mechanism, and thermodynamics. Powder Technology. 258, 20–31. https://doi.org/10.1016/j.powtec.2014.02.063
- Anggoro, D.D., Sumantri, I., Buchori, L., 2021. Indonesia's natural zeolite as an adsorbent for toxic gases in shrimp ponds. Journal of Ecological Engineering. 22(6), 202–208. https://doi. org/10.12911/22998993/137921
- Ansari, W., Harahap, H., Husin, A., 2021. Fixed-Bed Column Adsorption Performance For Ammonia Removal Using Adsorbent From Zeolite. IOP Conference Series: Materials Science And Engineering. 1122(1) 1–8. https://doi. org/10.1088/1757-899X/1122/1/012076
- Anh, N.T.V., 2024. Utilization of risk husk and alum sludge to produce an efficient adsorbent composite for recovery of nurtients from wastewater. Applied Science and Engineering Progress, 17(1), 6898. https://doi.org/10/14416/j.asep.2023.08.002
- Attia, A.A.M., Shouman, M.A.H., Khedr, S.A.A., Hassan, N.A., 2018. Fixed-bed column studies for the removal of Congo red using Simmondsia Chinensis (Jojoba) and coated with chitosan. Indonesian Journal of Chemistry. 18(2), 294–305. https:// doi.org/10.22146/ijc.29264
- Bish, D.L., Carey, B., 2001. Thermal behavior of natural zeolite. Reviews in Mineralogy and Geochemistry, 45(1), 403–452. https://doi.org/10.2138/ rmg.2001.45.13
- Dewi, E.M., Suryaningtyas, D.T., Anwar, S., 2017. Utilization of natural zeolites as Cu(II) and Zn(II) adsorbent. Journal of Tropical Soils, 21(3), 153–160. https://doi.org/10.5400/jts.2016.v21i3.153-160
- Elysabeth, T., Zulnovri, Ramayanti, G., Setiadi, Slamet., 2019. Modification of lampung and bayah natural zeolite to enhance the efficiency of removal of ammonia from wastewater. Asian Journal of Chemistry, 31(4), 873–878. https://doi. org/10.14233/ajchem.2019.21810
- Gea, S. Haryono, A., Andriayani, A., Sihombing, J.L., Pulungan, A.N., Nasution, T., Rahayu, R., Hutapea, Y.A., 2020. The effect of chemical activation using base solution with various concentrations

towards Sarulla Natural Zeolite. Elkawnie: Journal of Islamic Science and Technology, 6(1), 85–95. https://doi.org/10.22373/ekw.v6i1.6913

- Han, B., Butterly, C., Zhang, W., He, J., Chen, D., 2021. Adsorbent materials for ammonium and ammonia removal: A review. Journal of Cleaner Production. 283. https://doi.org/10.1016/j. jclepro.2020.124611
- Huang, J., Kankanamge, N.R., Chow, C., Welsh, D.T., Li, T., Teasdale, P.R., 2017. Removing ammonium from water and wastewater using cost-effective adsorbents: A review. Journal of Environmental Science. 63(19), 174–197. https://doi.org/10.1016/j.jes.2017.09.009
- Huang, X., Wang, N., Kang, Z., Yang, X., Pan, M., 2022. An investigation into the adsorption of ammonium by zeolite-magnetite composites. Minerals. 12(256), 1–14. https://doi.org/10.3390/ min12020256
- Husin, A., Aruan, F.H., Huda, A., Herlina, N., Manalu, S.P., 2024. Ammonia adsorption process using sarulla natural zeolite from North Sumatera, Indonesia. E3S Web of Conferences. 519(03028), 1–5. https://doi.org/10.1051/e3sconf/202451903028
- Kuldeyev, E., Seitzhanova, M., Tanirbergenova, S., Tazhu, K., Doszhanov, E., Mansurov, Z., Azat, S., Nurlybaev, R., Berndtsson, R., 2023. Modifying natural zeolites to improve heavy metal adsorption. Water, 15(12), 2215. https://doi.org/10.3390/215122215
- Liu, P., Zhang, A., Liu, Y., Liu, Z., Liu, X., Yang, L., Yang, Z., 2022. Adsorption mechanism of high-concentration ammonium by Chinese Natural Zeolite with Experimental Optimization and Theoritical Computation, Water, 14(15), 2413. DOI: 10.3390/w14152413.
- 17. Nagaraju, T.V., Sunil, B.M., Chaudhary, B., Prasad, C.D., Gobinath, R., 2023. Prediction of ammonia contaminants in the aquaculture ponds using soft computing coupled with wavelet analysis. Environmental Pollution, 331(2), 121924. https://doi. org/10.1016/j.envpol.2023.121924
- 18. Noelaka, Y.A.B., Kalla, E.B.S., Malelak, G.A., Rukman, N.K., 2018. Adsorption of methylene blue using acid activated green color natural zeolite from Ende-Flores, Indonesia. Rasayan Journal of Chemistry, 11(2), 494–504. https://doi.org/10.7324/ RJC.2018.1121994
- 19. Omitola, O.B., Abonyi, M.N., Akpomie, K.G., Dawodu, F.A., 2022. Adams-bohart, yoon-nelson, and thomas modeling of the fixed-bed continuous column adsorption of amoxicillin onto silver nanoparticle-maize leaf composite. Applied Water Science, 12(94), 1–9. https://doi.org/10.1007/ s13201-022-01624-4
- Patel, H., 2019. Fixed-bed column adsorption study: A comprehensive review. Applied Water Science, 9(45), 1–17. https://doi.org/10.1007/

s13201-019-0927-7

- Pratomo, S.W., Mahatmanti, F.W., Sulistyaningsih, T., 2017. Utilization of H₃PO₄ activated natural zeolite as an adsorbent of Cd(II) metal ions in solution. Indonesian Journal of Chemical Science, 6(2), 161–167 (in Indonesian).
- Putri, Sella A., Asnawati., Indarti, D. 2019. Optimization of Rhodamin B dyes adsorption on hemicellulose in dynamic systems. BERKALA SAINSTEK, 6(1), 1–6. https://doi.org/10.19184/bst.v7i1.9681(in Indonesian)
- 23. Radhika, R., Jayalatha, T., Rekha, K.G., Salu, J., Rajeev, R., Benny, K.G. 2018. Adsorption performance of packed bed column for the removal of perchlorate using modified activated carbon. Process Safety and Environmental Protection, 117, 350–362. https:// doi.org/10.1016/j.psep.2018.04.026
- 24. Selambakkannu, S., Othman, N.A.F., Bakar, K.A., Karim, Z.A., 2019. Adsorption studies of packed bed column for the removal of dyes using amine functionalized radiation induced grafted fiber. SN Applied Science, 1(175), 1–10. https://doi. org/10.1007/s42452-019-0184-2
- 25. Shaban, M., AbuKhadra, M.R., Nasief, F.M., El-Salam, H.M.A., 2017. Removal of ammonia from aqueous solutions, ground water, and wastewater using mechanically activated clinoptilolite and synthetic zeolite-a: Kinetic and equilibrium studies. Water, Air, & Soil Pollution, 228(450), 1–16. https://doi.org/10.1007/s11270-017-3643-7
- 26. Sintya, M., 2022. Improving the quality of brackish water using activated carbon and zeolite media. Environmental Health Journal Ruwa Jurai, 15(3), 124–129 (in Indonesian). https://doi.org/10.26630/ rj.v15i3.3073
- Statista. 2024. Production volume of farmed shrimp in Indonesia from 2011 to 2020. URL: https://www. statista.com/statistics/1230592/indonesia-productionvolume-of-farmed-shrimp/ Access on Jul 30, 2024.
- 28. Suryani, P.E., Candra, A.D., 2021. Application of chemical and physical activation methods on natural zeolites as metal adsorbents in the water purification process. SIMETRIS, 15(2), 5–7. (in Indonesian) https://doi.org/10.51901/simetris.v15i2.202
- Syauqiah, I., Amalia, M., Kartini, H.A., 2011. Analysis of time and stirrer speed variations in heavy metal waste adsorption process with activated carbon. INFO TEKNIK, 12(1), 1, 1–20. (in Indonesian)
- 30. Tong, D., Zhu, Z., Wu, J., Li, F., Shen, J., Cao, J., Tang, Y., Liu, G., Hu, L., Shi, W., 2023. Impacts of ammonia stress on different pacific whiteleg shrimp *Litopenaeus vannamei* families and the underlying adaptive mechanisms. Aquatic Toxicology, 259, 106549. https://doi.org/10.1016/j. aquatox.2023.106549

- 31. Tran, H.D., Phuc, H.N., Phuong, P.V.H., Thien, L.N.P., Nguyen, T.L., Tran, U.P.N., Dan, V.-N. 2024. A proposed model for breaking curves of methylene blue adsorption on biochar. Chemi, Biochem,. Eng. Q., 38(2), 153–164. https://doi.org/10.15255/ CABEQ.2023.2280
- 32. Wang, H., Gui, H., Yang, W., Li, D., Tan, W., Yang, M., Barrow, C.J., 2014. Ammonia nitrogen removal from aqueous solution using functionalized zeolite columns. Desalination and Water Treatment. 52: 753–758. https://doi.org/10.1080/19443994.2013.827316
- 33. Wati, L.A., 2018. Analyzing the Development of Indonesia Shrimp Industry. IOP Conference Series: Earth and Environmental Science. 137, 012101. https://doi.org/10.1088/1755-1315/137/1/012101
- 34. Zhu, Y., Chang, H., Yan, Z., Liu, C., Liang, Y., Qu, F., Liang, H., Vidic, R.D. 2024. Review of ammonia recovery and removal from wastewater using hydrophobic membrane distillation and membrane contactor. Separation and Purification Technology, 328, 125094. https://doi.org/10.1016/j. seppur.2023.125094