



## Optimization and Kinetic Study of Ende-Natural Zeolite as Candidates of Ammonia Adsorbent on Broiler Chicken Litter

Abner Tonu Lema<sup>1✉</sup>, Cytske Sabuna<sup>1</sup>, Yehezkiel Wila Balu<sup>2</sup>

<sup>1</sup>Livestock Feed Technology Study Program, Animal Husbandry Department, State Agricultural Polytechnic of Kupang, Jl. Prof. Dr. Herman Yohanes, Kupang, 85228, Indonesia

<sup>2</sup>Animal Feed and Nutrition Laboratory, Animal Husbandry Department, State Agricultural Polytechnic of Kupang, Jl. Prof. Dr. Herman Yohanes, Kupang, 85228, Indonesia

**Abstract.** Zeolite Natural Ende (ZNE) is a local material from Ende, East Nusa Tenggara which can be used as an adsorbent candidate to reduce environmental pollution due to poultry farm wastes. The purpose of this study is to obtain optimal conditions and adsorption kinetics of ZNE as an adsorbent in terms of absorbing NH<sub>3</sub>, water content, and neutralizing pH on broiler litter. This study consisted of 3 stages such as sample preparation, optimization of acid concentration, particle size, contact time, adsorbate concentration, as well as determination of ZNE-methylene blue adsorption kinetics. The results of analysis revealed that the best conditions are using 1 M H<sub>2</sub>SO<sub>4</sub>, particle size 80 mesh, contact time for 30 minutes with an adsorption capacity of 1.999 mg/g and methylene blue 80 ppm as an optimal condition. Furthermore, ZNE-methylene blue adsorption kinetics model is the second order type 1 kinetics by R<sup>2</sup> = 1, and also adsorption rate constant is 0.0019 g.mg<sup>-1</sup>.min

**Keywords:** Zeolite Natural Ende, adsorbent, ammonia, litter.

**Abstrak.** Zeolit alam Ende (ZAE) merupakan material lokal asal Ende, Nusa Tenggara Timur yang dapat digunakan sebagai adsorben pada campuran alas kandang untuk mengurangi pencemaran lingkungan akibat limbah peternakan unggas. Tujuan penelitian ini yaitu untuk memperoleh kondisi optimum dan kinetika adsorpsi ZAE sebagai adsorben dalam menyerap NH<sub>3</sub>, kadar air dan menetralkan pH pada litter ayam Broiler. Penelitian ini terdiri dari 3 tahapan yaitu preparasi sampel, optimasi parameter uji (konsentrasi asam, ukuran partikel, waktu kontak dan konsentrasi optimum adsorbat), dan penentuan kinetika adsorpsi ZAE-metilen blue. Hasil analisis menunjukkan bahwa kondisi optimum meliputi H<sub>2</sub>SO<sub>4</sub> 1 M, ukuran partikel 80 mesh, waktu kontak 30 menit dengan kapasitas adsorpsi sebesar 1,999 mg/g dan konsentrasi optimum metilen blue sebesar 80 ppm. Model kinetika adsorpsi metilen blue menggunakan adsorben ZAE adalah kinetika orde dua tipe 1 dengan nilai R<sup>2</sup> = 1 dan konstanta laju adsorpsi sebesar 0,0019 g.mg<sup>-1</sup>.menit. Zeolit alam Ende memiliki kemampuan adsorpsi yang baik sehingga dapat diaplikasikan sebagai material campuran pada alas kandang ayam broiler untuk mengurangi kadar amonia yang terlarut dalam urin dan feses.

**Kata kunci:** Zeolit Alam Ende, adsorben, amonia, alas kandang.

Received: June 2<sup>nd</sup>, 2022, Accepted: August 2<sup>nd</sup>, 2022

Citation: Lema, AT., Sabuna, C, and Bau, YW. (2022). Optimization and Kinetic Study of Ende-Natural Zeolite as Candidates of Ammonia Adsorbent on Broiler Chicken Litter. *KOVALEN: Jurnal Riset Kimia*, 8(2): 150-157.

### INTRODUCTION

The problem faced by the farmers in the management of broiler chicken maintenance is the smell of ammonia from the litter which pollutes the environment. Ammonia is one of

the gases which is resulting from the decomposition of nitrogenous waste in excreta, such as uric acid, unabsorbed protein, amino acids and other non-protein nitrogen (NPN) compounds due to the activity of microorganisms in feces. In addition, ammonia gases produced can reduce the performance of

✉ Corresponding author  
E-mail: [abner\\_t.lemma@yahoo.com](mailto:abner_t.lemma@yahoo.com)

<https://doi.org/10.22487/kovalen.2022.v8.i2.15914>



poultry, and as a medium for the spread of disease (Riza et al., 2015). The presence of chicken manure with high strongly humidity supports the proliferation of bacteria. Ammonia levels can increase if the cage ventilation is poor, the air temperature is extreme, and the cage contents are too dense. High levels of ammonia will greatly disrupt the environment as well as reduce livestock productivity. As a result, production costs will increase because the resistance of the chickens to diseases will decrease such as respiratory diseases, chicken colds and epilepsy. In addition, the health and comfort of workers will be disturbed due to bad environmental conditions (Riza et al, 2015). Air and litter contaminated with  $\text{NH}_3$  and  $\text{H}_2\text{S}$  gases can cause chickens health problems, particularly respiratory disorders that cause Chronic Respiratory Disease (CRD) and increase the activity of the Newcastle Disease (ND) virus. If the concentration of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  gas in the cage exceeds 0.05%, it can cause chicken death (Ibrahim & Allaily, 2012).

To overcome the problem of high levels of ammonia and humidity in the cage, natural zeolite can be used as an adsorbent in the cage litter. Nowadays, farmer use zeolite as one of the mixed material on litter. However, the limitation is without modification, it has not been effective due to the limited number of active sites or pores (Ibrahim & Allaily, 2012). Natural zeolites are silica-alumina minerals with a porous, channel-forming framework structure, and are constructed by primary tetrahedral units  $[\text{SiO}_4]^{4-}$  and  $[\text{AlO}_4]^{3-}$ . Monovalent and divalent cations can be used as cation exchangers in the adsorption process. The porous structure of natural zeolite produces a large surface area, so zeolite has a high adsorption capacity (Rendo, 2021). Zeolites

also have an open three-dimensional framework containing channels and cavities, which are filled with metal ions, usually alkali or alkaline earth metals and freely moving water molecules (Ginting, 2017).

The activation of natural zeolite can be processed by the chemical and physical treatments. An acid treatment can be used as an activator to chemically remove the impurity minerals. Zeolite modification was carried out to obtain different forms of cations and framework compositions using ion exchange, dealumination, and isomorphous substitution mechanisms. While physical activation is carried out by reducing the particle size, sieving, and calcining to remove the organic impurities, enlarging and expanding the pore surface (Lestari, 2010).

On the other hand, the use of synthetic zeolite powder by 25% and 50% can reduce ammonia levels by  $0.956 \text{ mg/m}^2$ . In addition, it can also improve feed palatability and weight gain of livestock and reduce broiler mortality (Ibrahim and Allaily, 2012). As the research reported by Ngapa et al. (2016) regarding the structure of the natural zeolite Ende, by modifying the pore structure of the zeolite using 3 M HCl and resulting in an increased cation exchange capacity (CEC) of up to 75%. Furthermore, Ende-natural zeolite is also more resistant to heat so the calcination process up to  $600^\circ\text{C}$  does not damage the structure of natural zeolite, in contrast to synthetic zeolite which is not resistant to heat (Ngapa et al., 2016). Therefore, this work was focusing on optimal conditions and kinetic study of natural zeolite before applied to broiler chicken litter as ammonia adsorbent. Furthermore, this study could be essential information in terms of developing adsorbent in Indonesia.

## MATERIAL AND METHODS

### Materials

The natural zeolite materials used in the study was taken from Nangapenda, Ende district-East Nusa Tenggara, H<sub>2</sub>SO<sub>4</sub> concentrated (p.a), methylene blue (Merck, Germany), filter paper, 96% ethanol (Merck, Germany), and aquabides. The tools used were: sample grinder, porcelain mortar, sieve size of 20, 40, 60, and 80 mesh, hotplate stirrer, furnace, oven, desiccator, cuvette, universal pH meter, measuring flask, and other glassware.

### Instrumentation

Spectrophotometer UV-Vis single beam (Cecil 2021) is used to measure the absorbance of metilen blue.

### Procedure

#### Natural zeolite preparation

500 gram of natural zeolite was ground using a grinder and filtered with a fineness level of 20, 40, 60, and 80 meshes. The zeolite was then washed using aquabides and dried at 110 °C for 4 hours.

#### Determination of optimum concentration of H<sub>2</sub>SO<sub>4</sub>

Optimization of the concentration of H<sub>2</sub>SO<sub>4</sub> using a concentration variation of 1; 3; and 5 M to determine the concentration of H<sub>2</sub>SO<sub>4</sub> which gives the highest absorption. A total of 1 g of zeolite with a particle size of 80 meshes was added with 15 mL of 80 ppm methylene blue solution. The solution was agitated using a shaker and centrifuged at 1500 rpm for 30 minutes. The separated filtrate was measured for absorbance at 664 nm as the maximum wavelength (Ngapa & Ika, 2020). The highest absorption results will be used as the optimum concentration to activate 4 types of zeolite particle sizes (20, 40, 60, and 80 mesh).

#### Optimum particle size determination

A total of 1 gram of each natural zeolite particle size 20, 40, 60, and 80 mesh were added with 25 mL of optimum concentration H<sub>2</sub>SO<sub>4</sub>, shaken at room temperature for 15 minutes. The filtered filtrate was measured absorbance at 664 nm. The highest absorbance is the optimum particle size.

#### Optimum contact timing

A total of 1 gram of natural zeolite with optimum particle size was added with 25 mL of optimum H<sub>2</sub>SO<sub>4</sub>, shaken at room temperature with contact times of 15, 30, 60, 90, 120, and 150 minutes. The filtered filtrate was measured absorbance at 664 nm. The highest absorbance is the optimum contact time.

#### Determination of the optimum concentration of adsorbate

Each of 0.5, 1, 1.5, 2, 2.5, 3, 3.5, and 4 mL of 1000 ppm methylene blue solution was added with 1 gram ZNE and shaken at room temperature at the optimum contact time. The filtered filtrate was measured absorbance at 664 nm. The highest absorbance was the optimum concentration of methylene blue.

The adsorption capacity can be calculated by the formula:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad \dots (1)$$

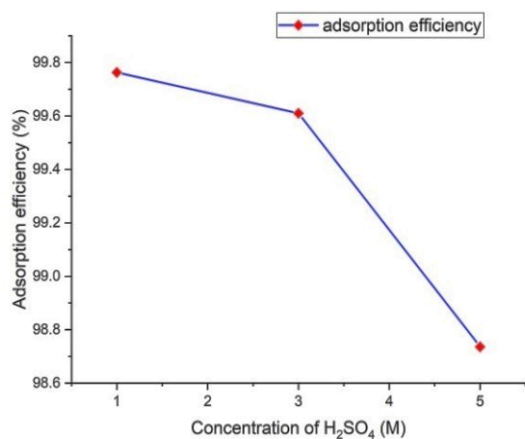
Where:  $q_e$  is adsorption capacity (mg/g);  $v$  is volume of solution (L);  $C_0$  is initial concentration of methylene blue ion (mg/L);  $C_e$  is initial concentration of methylene blue ion in equilibrium (mg/L);  $m$  is mass of natural zeolite (grams).

## RESULT AND DISCUSSION

### Activation of Natural Ende Zeolite (ZNE)

The ZNE activation process was carried out by adding H<sub>2</sub>SO<sub>4</sub> with concentrations of 1,

3, and 5 M. The purpose of the activation was to dissolve the trapped valence metals of 1 and 2 and block the surface of the zeolite pores and to remove impurities. The usage of these 3 variations of acid concentration was to obtain the optimum acid concentration in the adsorption process. The measurement of the interaction between the adsorbent and the adsorbate was carried out at the maximum wavelength because at the maximum wavelength gives the highest absorption value and to reduce errors in spectrophotometric measurements (Lema *et al.*, 2014). The highest efficiency for the minerals adsorption occurred when the concentration of  $H_2SO_4$  was 1 M (Figure 1). If an acid concentration ( $H_2SO_4 > 1$  M) is too high, it will damage the pore structure on surface (Ngapa and Gago, 2019). On top of that, other research revealed that the using of HCl 1 M showed the surface area of natural zeolite becomes wider than using lower acid concentration (HCl 0.2 M) (Ismettulloh *et al.*, 2019).

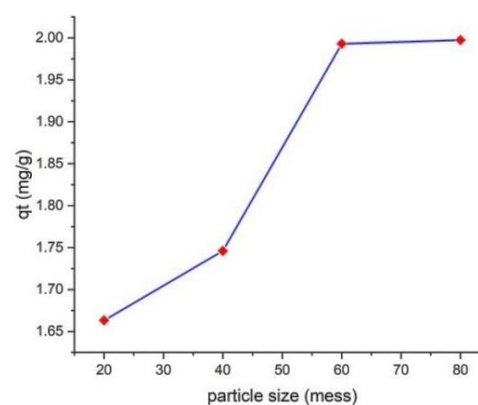


**Figure 1.** Effect of concentration of  $H_2SO_4$  on efficiency Adsorption

### Optimum Particle Size

Variations in particle size used are ZNE 20; 40; 60 and 80 mesh. The optimization results show the highest methylene blue adsorption process at 80 mesh size ZNE

(Figure 2). Theoretically, the surface area of the zeolite will be larger if the particle size of the adsorbent is smaller so that more methylene blue is adsorbed on the surface of the zeolite. The purpose of the ZNE particle size limit at 80 mesh is that the particles are able to interact with the size of the rice husk so that the zeolite does not pass on the floor. The choice of rice husk as one of the mixed ingredients with zeolite because the husk has the ability to absorb water and provide air cavities in the litter (Anwar *et al.*, 2014). In addition, if the particle size of zeolite is too small ( $> 80$  mesh), it may be consumed by the chickens.

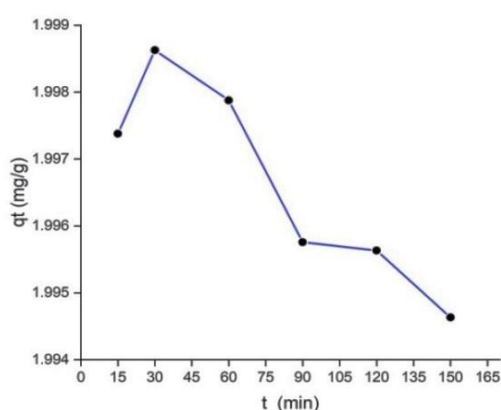


**Figure 2.** Effect of particle sizes on ZNE adsorption efficiency

### Optimum Contact Time

Contact time affects the amount of adsorbates that is absorbed, due to differences in the ability of the adsorbent to absorb different adsorbates. Determination of the contact time that produces the maximum adsorption capacity occurs at equilibrium. Determination of contact time was carried out by interacting ZNE with methylene blue at intervals of 15, 60, 90, 120, and 150 minutes. The interaction results gave the highest absorption time at 30 minutes. Figure 3 show the interaction time above the 30 minutes of the zeolite was saturated that the adsorption capacity decreased until the 150

minutes. Equilibrium conditions was reached no more than 30 minutes, after the amount of adsorbate adsorbed does not significantly change by time. This is because the collision between the adsorbate and the adsorbent continues to increase, causing a decrease in adsorption capacity. At equilibrium conditions, the surface of the adsorbent is saturated in which the addition of contact time will not affect the adsorption process and it will not increase the amount of adsorbate (Maryudi *et al.*, 2021).

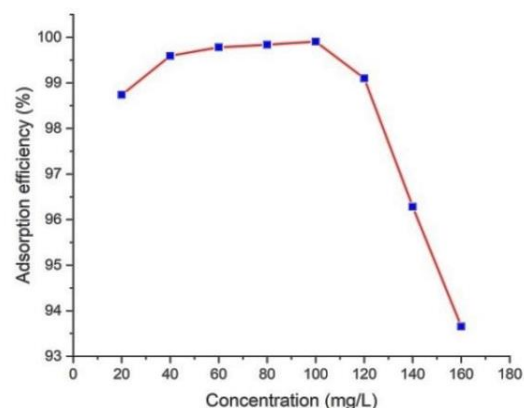


**Figure 3.** Effect of contact time on adsorption capacity of adsorbate

### Optimum Concentration of Adsorbate

The interaction between ZNE and methylene blue at various concentrations showed the ability to absorb adsorbate. According to figure 3 that there is an increase in absorption from a concentration of 20 ppm to 100 ppm. This is occurred due to the number of available zeolite active sites exceeds the concentration of methylene blue that the adsorption process runs effectively (Caparkaya & Cavas, 2008). However, when the concentration of adsorbate above 100 ppm, adsorption efficiency decreased significantly because all zeolite active sites were filled so the addition of methylene blue concentration could not be absorbed properly (Ngapa & Ika, 2020).

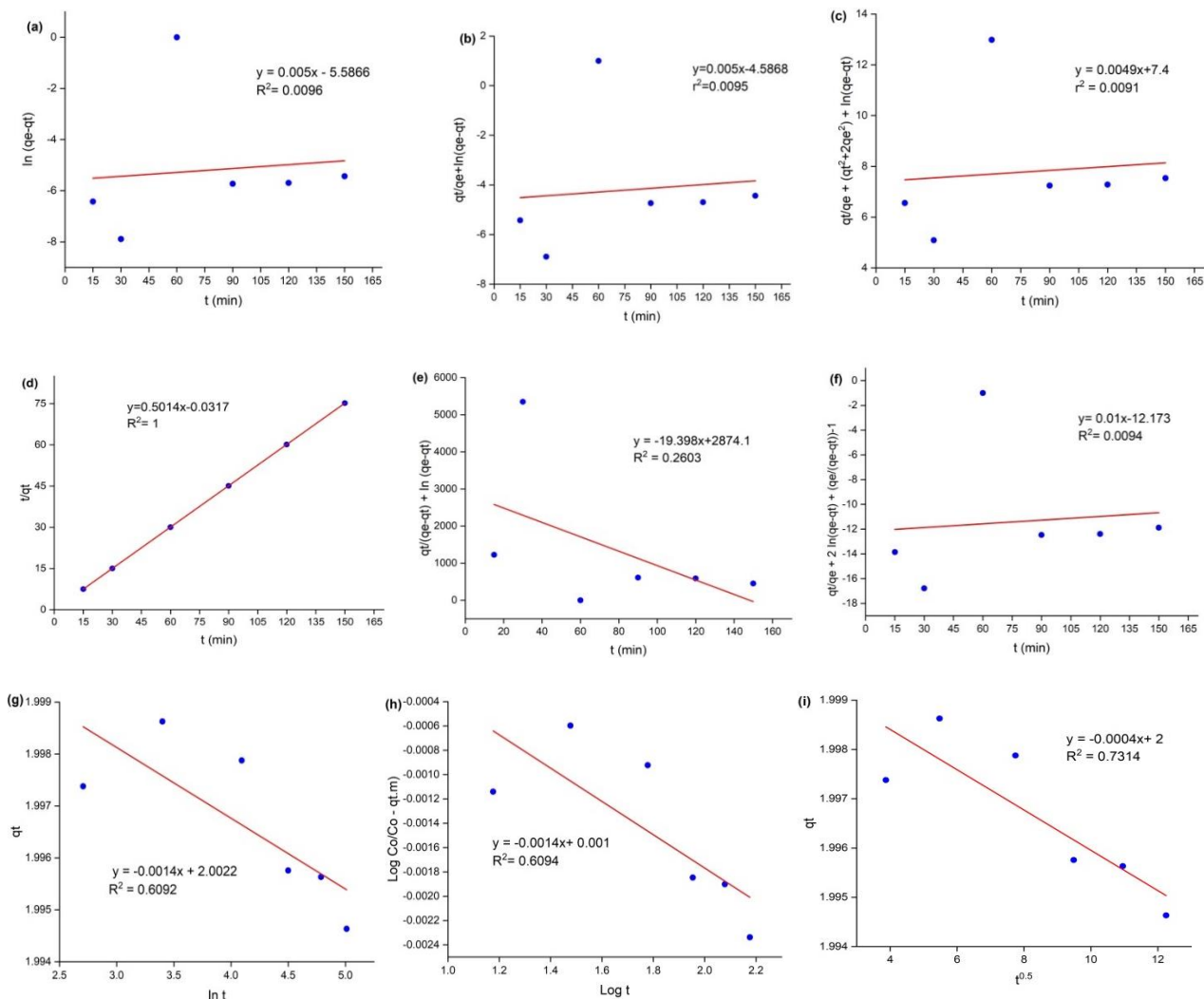
This is due to the zeolite active sites were saturated with methylene blue and even the bonds were released. The result showed that there was a decreased intensity of ZAE-methylene blue complex colour which is simultaneously by dropped dramatically of absorbance from 120 ppm to 160 ppm (Figure 4).



**Figure 4.** Adsorption efficiency at various concentrations of methylene blue

### Methylene Blue Adsorption Kinetics using Ende Natural Zeolite (ZNE)

The ability of zeolite to absorb the adsorbate depends on the characteristics of the zeolite. Determination of the adsorption kinetics model aims to determine the amount of methylene blue adsorbed on the ZNE as an adsorbent at various contact times of 15, 30, 60, 90, 120, and 150 minutes with an optimum contact time of 30 minutes. The kinetic models in this study are first-order kinetics type 1, first-order kinetics type 2, first-order kinetics type 3, second-order kinetics type 1, second-order kinetics type 2, second-order kinetics type 3, Elovich kinetics, Bangham kinetics and Weber-Morris intra particle diffusion (Wang & Guo, 2020). The type of kinetics and the results of adsorption capacity are shown in Figure 5 and Table 1.



**Figure 5.** Adsorption kinetics model curve (a) first-order kinetics type 1, (b) first-order kinetics type 2, (c) first-order kinetics type 3, (d) second-order kinetics type 1, (e) second-order kinetics type 2, (f) second-order kinetics of type 3, (g) Elovich kinetics, (h) Bangham kinetics, and (i) Weber-Morris kinetics of intraparticle diffusion.

**Table 1.** Adsorption capacity of natural zeolite against methylene blue at various contact time

Contact Time (minute)	Capacity Adsorption (mg/g)	Absorption Efficiency (%)
15	1.997	99.87
30	1.999	99.93
60	1.998	99.89
90	1.996	99.79
120	1.996	99.78
150	1.995	99.73

The adsorption process of methylene blue using ZNE allows a second-order kinetic model of type 1. This can be seen from the value of  $R^2 = 1$ . The second-order kinetic model of type 1 indicates that the adsorption capacity is proportional to the number of active sites of the adsorbent (Sharifipour *et al.*, 2015). The adsorption rate constant of methylene blue using ZNE adsorbent was  $0.0019 \text{ g} \cdot \text{mg}^{-1} \cdot \text{minutes}$ , meaning that as much as 0.0019 g of adsorbent was able to adsorb 1 mg of adsorbate in 1 minute. On the other hand, the adsorption rate is also depends on the



characteristics of the zeolite (Wang & Guo, 2020; Wu et al., 2013).

Moreover, other research showed that Manganese-TiO<sub>2</sub> zeolite 20% reduced CO levels by 58.00%, Hydrocarbon by 45.51% and Pb by 93.51% (Widihati et al., 2021). Therefore, modification of natural zeolite can be applied to reduce various gasses such as ammonia, CO<sub>2</sub>, CH<sub>3</sub>, and H<sub>2</sub>S on closed system chicken coop.

## CONCLUSION

The optimum condition of Ende-natural zeolite (ZNE) is activated by 1 M H<sub>2</sub>SO<sub>4</sub>, particle size of 80 mesh, and interaction time of 30 minutes, adsorption capacity of 1.999 mg.g<sup>-1</sup>. The optimum concentration of methylene blue is 80 ppm. Methylene blue adsorption kinetics model using ZNE is second order type 1 kinetics by R<sup>2</sup>=1 and adsorption rate constant of 0.0019 g.mg<sup>-1</sup> minutes. Thus, Ende-natural zeolite can be used as a candidate adsorbent on broiler litter mixtures to reduce dissolved ammonia levels, water content and neutralization pH on litter.

## ACKNOWLEDGMENT

Funding: This project was supported by the Center of Research and Community Service (P3M) of State Agricultural Polytechnic of Kupang [grant numbers: 03/P3M/SP DIPA. 023.18.2.677616/2021].

## REFERENCES

- Anwar, R., Nova, K. and Kurtini, T. (2014). Pengaruh Penggunaan Litter Sekam, Serutan Kayu, dan Jerami Padi terhadap Performa Broiler di Closed House. *Jurnal Ilmiah Peternakan Terpadu*, 2(3).
- Caparkaya, D. and Cavas, L. (2008). Biosorption of Methylene Blue by a Brown Alga *Cystoseira barbatula* Kützing. *Acta Chimica Slovenica*, 55(3).

- Ginting, E. M. (2017). Struktur dan morfologi nano komposit campuran zeolit abu sekam padi. *Jurnal Material dan Energi Indonesia*, 7(01): 19–24.
- Ibrahim, S. and Allaily, A. (2012). Pengaruh Berbagai Bahan Litter Terhadap Konsentrasi Ammonia Udara Ambient kandang dan Performan Ayam Broiler. *Jurnal Agripet*, 12(1): 47–51.
- Ismettulloh, M. et al. (2019). Modifikasi Zeolit Alam Bayah Menggunakan Asam dan Pengaplikasiannya Dalam Pengurangan Amonium Pada Kolam Ikan Bandeng. *Jurnal Integrasi Proses*, 8(1): 7–13.
- Lema, A. T., Sulistyarti, H. and Atikah, A. (2014). Development of Spectrophotometric Methods for Iodide Determination Using Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) as Oxidizing. *Natural B, Journal of Health and Environmental Sciences*, 2(4): 309–316.
- Lestari, D. Y. (2010). Kajian modifikasi dan karakterisasi zeolit alam dari berbagai negara. in *Prosiding Seminar Nasional Kimia dan Pendidikan Kimia*, pp. 1–6.
- Maryudi, M., Aktawan, A. and Amelia, S. (2021). Pengolahan Limbah Pewarna Metilen Biru Menggunakan Arang Aktif dan Zeolit Aktif dengan Katalis Fe dan Oksidator Hidrogen Peroksida. *Jurnal Riset Kimia*, 12(2).
- Ngapa, Y. D. and Gago, J. (2019). Adsorpsi Ion Pb (II) Oleh Zeolit Alam Ende Teraktivasi Asam: Studi Pengembangan Mineral Alternatif Penjerap Limbah Logam Berat. *Cakra Kimia*, 7(2): 84-91
- Ngapa, Y. D. and Ika, Y. E. (2020). Optimasi Adsorpsi Kompetitif Pewarna Biru Metilena dan Metil Oranye Menggunakan Adsorben Zeolit Alam Ende-Nusa Tenggara Timur (NTT). *Indonesian Journal of Chemical Research*, 8(2): 151–158.
- Ngapa, Y. D., Sugiarti, S. and Abidin, Z. (2016). Hydrothermal transformation of natural zeolite from Ende-NTT and its application as adsorbent of cationic dye. *Indonesian Journal of Chemistry*, 16(2): 138–143.
- Rendo, D. (2021). Adsorption of Methylene Blue Dye using Fe<sub>3</sub>O<sub>4</sub> Magnetized Natural Zeolite Adsorbent. *Jurnal Kimia Sains dan Aplikasi*, 24(2): 51–57.
- Riza, H., Wizna, W. and Rizal, Y. (2015). Peran Probiotik dalam Menurunkan Amonia Feses Unggas. *Jurnal Peternakan*

*Indonesia (Indonesian Journal of Animal Science)*, 17(1): 19–26.

- Sharifipour, F. et al. (2015). Kinetics and thermodynamics of lead adsorption from aqueous solutions onto Iranian sepiolite and zeolite. *International Journal of Environmental Research*, 9(3): 1001–1010.
- Wang, J. and Guo, X. (2020). Adsorption kinetic models: Physical meanings, applications, and solving methods. *Journal of Hazardous Materials*, 390: 122156.
- Widihati, I. A. G., Apriliyanto, I. and Sibarani, J. (2021). Karakterisasi Zeolit Mangan Termodifikasi TiO<sub>2</sub> Serta Aplikasinya Sebagai Filter Gas Buang Kendaraan Bermotor Dalam Penurunan Kadar Gas CO, HC, dan Pb. *Jurnal Kimia (Journal of Chemistry)*, 15(1): 107–114.
- Wu, Q. J. et al. (2013). Effects of clinoptilolite and modified clinoptilolite on the growth performance, intestinal microflora, and gut parameters of broilers. *Poultry Science*, 92(3): 684–692.