Utilization of Yogyakarta natural zeolites to reduce NH₄ and NO₂ levels in shrimp pond water and its kinetic rate study

D D Anggoro¹, L Buchori¹, I Sumantri¹, Ivan¹, D A B Sejati¹, H Oktavianty¹
¹Department of Chemical Engineering, Diponegoro University, Semarang, 50275, Indonesia

E-mail: anggororphd@gmail.com

Abstract. Natural zeolite is an unique crystal that has a very small and uniform pore size when compared to other adsorbents, such as activated carbon and silica gel. This study aims to determine the potential of natural zeolite as an adsorbent to absorb toxic gases in pond water, especially shrimp ponds and to study its kinetics rate of NH₄ and NO₂ adsorption. This study consisted of two stages: activated zeolite using NaOH, and tested the absorption power of NH₄ and NO₂ gases. Zeolite was activated using NaOH where 25 grams of zeolite were mixed with 0.5N NaOH and heated for 2 hours at 70°C, then stirred and dried in an oven at 110°C for 4 hours. Then zeolite was cooled in a desiccator. The results of NH₄ and NO₂ gas adsorption showed that natural zeolites can reduce NH₄ and NO₂ gas levels in shrimp pond water. The rate constant of pseudo-second-order, and the initial adsorption rate at any given time t, can be predicted from the equation which is full zeolite obtained the best perform of NH₄ and NO₂ adsorption.

1. Introduction

Development of cultivation systems from traditional to intensive with the majority shrimp ponds have potential towards increasing environmental pollution. Less optimal utilization of excessive feed will cause accumulation of organic matter. Decomposition of organic matter requires oxygen in the process, so that the availability of oxygen for the biota in it is reduced. If this happens continuously it will cause death for shrimp and other biota. Pollution materials that are difficult to decompose by microorganisms also cause hoarding and result in damage to the environment which will directly disrupt organisms that live in these environments. Organic pollution materials that function as fertilizers are actually detrimental due to algae blooms and aquatic plants causing oxygen competition in the waters. The above factors are the cause of the decline in the body's resistance to the attack of the disease because of the poor quality of the environment, if this is left continuously then mass death will occur so that the population will decline [1].

Traditional methods for nitrogen removal from wastewater are denitrification, nitrification, chemical coagulation, adsorption, selective ion exchange, ammonia stripping, electrodialysis, filtration, reverse osmosis [2, 3, 4, 5]. Removal processes of dissolved nitrogen compounds, can vary. For intensive RAS (Return Activated Sludge), the most common practice involves utilizing nitrifying bacteria to convert ammonia-nitrogen to nitrate-nitrogen [6]. The rate limiting step of this process is the oxidation of ammonia [7]. Incomplete nitrification occurs when a lack of NOB (Nitrite Oxidizing Bacteria) productivity is present, leading to increased concentrations of nitrite. The adsorption process
is more widely used in industry because it has several advantages, which are more economical and also does not cause toxic side effects and is able to eliminate organic materials. Adsorption is a process that occurs when molecules from substances liquid or gas accumulates on a solid / liquid surface, forming a thin layer formed from molecules or atoms. The most important thing in the adsorption process is the selection of a good type of adsorbent [6].

The adsorption process of solutions theoretically generally lasts longer than the adsorption process on gas, steam or pure liquid [8]. This is due to the adsorption of the solution involving competition between the solution components and the adsorption site. The solution adsorption process can be estimated qualitatively from the polarity of the adsorbent and the constituent components of the solution. The tendency of polar adsorbents to more strongly absorb polar adsorbates than non-polar adsorbates, and vice versa. The solubility of the adsorbate in the solvent is the determining factor in the adsorption process, generally the hydrophilic substance is difficult to adsorb in a dilute solution. Basically, an adsorbent must have a high specific surface area, which has small diameter pores so that the adsorbate retention process by the adsorbent takes place more effectively. Specifically, the pore size also determines the adsorption of a particular compound in solution. If the adsorbent's pore size gets smaller, the adsorption capacity is greater, assuming that the adsorbed component can enter the porous cavity. The greater number of adsorbents will provide a larger surface area for the adsorbate to be desorbed. In addition, the more the amount of adsorbent will also provide greater opportunity for contact with the adsorbate molecules [9].

One of the most potential adsorbents is zeolite. Zeolite has several properties such as having dehydration properties, high cation exchange, a good catalyst, and as an agent for other compounds [10]. Increased efficiency or optimization of zeolites as adsorbents can be done through activation. The activation process aims to cleanse the pore surface, remove disturbing compounds and increase the specific surface area [11]. At the activation stage, the adsorbent is first soaked using an activating material, including HCl, HNO₃, H₂SO₄ and H₃PO₄ [12].

This study aims to improve the quality of water using natural zeolite as an adsorbent so that the levels of NH₃ and NO₂ contained in water can be reduced and safe for shrimp breeding and also to aims kinetics rate of NO₂ and NH₃ adsorption using zeolite catalyst. In this study, filters were made from PVC pipes with a pipe length of 100 cm and a diameter of 6 inches (15.24 cm). The results of this study are expected to reduce the level of Fe to 96% and Mn decreased to 84.3%.

2. Experimental

2.1 Zeolite Activation
Zeolite is activated using NaOH where 25 grams of zeolite are mixed with 0.5N NaOH and heated for 2 hours at 70°C while stirring and then dried in an oven at 110°C for 4 hours. The zeolite is then cooled in a desiccator. After drying, zeolite is ready for use. This study used 3 variations of zeolite, volume zeolite 1/3 part of pipe, volume zeolite 2/3 part of pipe and full volume of zeolite that were filled in the pipe of filter.

2.2 Nitrite Levels Analysis
Analysis of nitrite levels was carried out using Diazotasi-Spectrofotometry method. In this study, samples with sulfanilic acid and N- (1-Nepthyl ethylene diamin) dihydrachloride in an acidic atmosphere (pH 2 - 2.5) formed a complex compound, then placed on a spectrophotometer to be analyzed at a wavelength of 420 nm.

2.3 Ammonium Levels Analysis
Analysis of ammonium levels was carried out by the Nessler-Spectrophotometry method. In this analysis, the sample in an alkaline atmosphere is reacted with Nessler reactants to form complex compounds that are yellow to brown. The intensity of the color that occurs is measured its absorbance at a wavelength of 420 nm.
3. Results and Discussion

3.1. NH₄ and NO₂ decreasing results

Figure 1 shows that the NH₄ concentration in shrimp pond water decreased from 300 minutes in all the amount of zeolite used. In the use of 25 grams a decrease in NH₄ concentration from 4.276 ppm to 3.879 ppm or around 9.284%. On the use of 50 grams and 100 grams there was a decrease in NH₄ concentration of around 15.084% and 18.569% respectively. This shows that the more amount of zeolite used, the greater the amount of NH₄ gas adsorbed.

![Figure 1. Decrease in NH₄ concentration with different amounts of zeolite](image1.png)

While Figure 2 shows that the NO₂ concentration in shrimp pond water decreased from 300 minutes in all the amount of zeolite used. In the use of 25 grams a decrease in NO₂ concentration from 0.457 ppm to 0.354 ppm or around 22.538%. On the use of 50 grams and 100 grams there was a decrease in NO₂ concentration of around 33.917% and 40.700% respectively. This shows that the more amount of zeolite used, the greater the amount of NO₂ gas adsorbed.

![Figure 2. Decrease in NO₂ concentration with different amounts of zeolite](image2.png)
3.2. Kinetics rate of NH\textsubscript{4} and NO\textsubscript{2} adsorption
There are many mathematical models are reported in the literature, all attempting to describe quantitatively in the kinetic behaviour during the adsorption process. Among these models, the pseudo-first-order, pseudo-second-order and intraparticle diffusion model were used to test kinetic experimental data.

3.2.1. Pseudo-second-order model
The rate constant of pseudo-second-order adsorption is determined from the following equation given by Lagergren [14, 15]:

\[
\frac{1}{C_A} - \frac{1}{C_{A0}} = k \cdot t
\]  

(1)

where, C\textsubscript{A} and C\textsubscript{A0} are the amounts of NH\textsubscript{4} and NO\textsubscript{2} adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k (min\textsuperscript{-1}) is the rate constant of the pseudo-second-order adsorption.

Results of k value for NH\textsubscript{4} adsorption can be shown in table 1 below.

| Zeolite | NH\textsubscript{4} before | NH\textsubscript{4} after | K     | R\textsuperscript{2} |
|---------|-------------------------|------------------------|-------|-----------------|
| Full    | 4.276                   | 3.435                  | 0.000188 | 0.98717        |
| 2/3     | 4.276                   | 3.581                  | 0.000138 | 0.99194        |
| 1/3     | 4.276                   | 3.824                  | 0.000072 | 0.98273        |

Results of k value for NO\textsubscript{2} adsorption can be shown in table 1 below.

| Zeolite | NO\textsubscript{2} before | NO\textsubscript{2} after | K     | R\textsuperscript{2} |
|---------|-------------------------|------------------------|-------|-----------------|
| Full    | 0.457                   | 0.222                  | 0.004441 | 0.89637        |
| 2/3     | 0.457                   | 0.250                  | 0.003601 | 0.98858        |
| 1/3     | 0.457                   | 0.297                  | 0.002010 | 0.98002        |

Table 1 and table 2 showed that the utilization of full zeolite obtained the higher adsorption of NH\textsubscript{4} and NO\textsubscript{2} gases. It means that the more zeolites are used, the more NH\textsubscript{4} and NO\textsubscript{2} gases are adsorbed. It is because of the activated zeolite has a surface area and acidity that is easily modified so it can absorb more NH\textsubscript{4} and NO\textsubscript{2} gases because the framework of the zeolite has been substituted with ions from the gas.

4. Conclusion
Full zeolite utilization obtained the best perform of NH\textsubscript{4} and NO\textsubscript{2} adsorption, respectively gave a decrease in the concentration of 18.569% NH\textsubscript{4} and 40% NO\textsubscript{2}. Adsorption kinetic data were analysed using the pseudo-second-order model. The advantage of using pseudo-second-order model is that the adsorption capacity, the rate constant of pseudo-second-order, and the initial adsorption rate at any given time t, can be predicted from the equation that respectively obtained 0.000188 and 0.004441 of k value for NH\textsubscript{4} and NO\textsubscript{2}.

Acknowledgements
The authors gratefully acknowledge the financial support received in the form of a research grant from in addition to APBN LPPM RKAP Diponegoro University Fiscal Year 2018.
References

[1] Kilawati Y and Maimunah Y 2015 Research Journal of Life Science 2(1) 50–59
[2] Tchobanoglous G 1979 Wastewater Engineering: Treatment Disposal Reuse (New York: McGraw-Hill, Inc.) 2nd ed. p. 88
[3] Henze M 1995 Nutrient removal from wastewater In New World Water (London: Sterling Publications Limited) p.114
[4] Bae B, Juang Y, Han W and Shin H 2002 Water Res. 36 3330-3340
[5] Lin S H and Wu C L 1996 Water Res. 30(8) 1851–1857
[6] Crab R, Defoirdt T, Avnimelech Y, and Verstraete W 2005 Aquaculture 270 1-14
[7] Vadivelu V, Keller J, and Yuan Z 2007 Water Science & Techno. 56(7) 89-97
[8] Rezaei F, and Webley P 2010 Sep. Purif. Technol. 70 243-256
[9] Gonzales M D, Cesteros Y, and Salagre P 2011 Micro. Meso. Mater. 144 162-170
[10] Pratomo S W, Mahatmanti F W, and Sulistyaningsih T 2017 Indo. J. Chem. Sci. 6(2) 104-109
[11] Kundari N A, Susanto A and Prihatiningsih M A 2010 Prosiding Seminar nasional VI SDM Teknologi nuklir Yogyakarta, 18 November 2010
[12] Emelda, L, Putri, S M, and Ginting, S 2013 Jurnal Rekayasa Kimia dan Lingkungan 9(4) 166-172
[13] Lagergren, S 1898 K. Sven. vetensk.akad. handl. 24(4) 1–39
[14] Ho, Y S 2004 Scientometrics 59(1) 171–177