Fixed-bed column adsorption performance for ammonia removal using adsorbent from zeolite

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Abstract. A study on the performance of fixed-bed column adsorption using natural zeolite Sarulla for ammonia removal has been carried out. The effect of important parameters namely bed height on the breakthrough curve and adsorption performance has been investigated in laboratory scale experiments. The study results show that the adsorption efficiency increases with increasing bed height. These results reveal that the throughput volume of aqueous solution increases with increasing bed height, due to the availability of more adsorption sites and a longer time to reach saturation. Adsorption kinetics were analyzed using the Thomas and Yoon and Nelson kinetics models. The kinetics data can be described well using these two models. The maximum adsorption capacity \( q_0 \) was determined using the Thomas kinetics model, the ammonia value was 279.3589 mg / g. However, the study results show that the value of \( q_0 \) decreases with increasing ammonia bed height. For Yoon and Nelson's models, the rate constant decreases with increasing bed height. The length of time required for 50% of the breakthrough increases with increasing bed height. The kinetics data can be correlated well using both models.

1. Introduction

Shrimp is a type of aquaculture commodity in Indonesia. Until the end of 2017, Indonesia had three million hectares of potential for shrimp ponds. The land has not been fully utilized optimally. In terms of volume, shrimp commodity in 2017 reached 390,000 tons with an export value of 1.47 billion US $. This large value and volume makes shrimp a commodity with a contribution of 33% of the total export value of Indonesian fishery products [1]. Shrimp ponds with the number of shrimp 750-1250 per m\(^2\) contain a total chemical oxygen demand of 1593 mg/L, total solid 33.1 g/L, ammonia 83 mg/L [2].

This very intensive shrimp cultivation can actually reduce the quality of coastal waters in several countries, especially in countries with the world’s largest number of fishery production, such as Thailand, Indonesia, the Philippines, Japan, and Mexico [3].

One of the chemicals that is quite disturbing to the environment is ammonia, which can be in the free form in the form of NH\(_3\) gas or dissolved in water as a solution of ammonium hydroxide (NH\(_4\)OH). Naturally, ammonia can be formed from the decomposition of proteins in waste or organic waste, so that in landfills, waste storage, livestock cages, and aquaculture ponds an unpleasant odor arises from ammonia. Besides smelling bad, the presence of ammonia gas in the air can also pollute the environment and cause health problems for humans who often breathe ammonia. Ammonia also dissolves easily in water, increasing the pH of the water to become alkaline, so that the water becomes polluted. The aquatic environment in fish / shrimp ponds is usually also polluted by dissolved ammonia as a result of the decomposition of fish / shrimp food scraps. Therefore, it is necessary to
look for ways to prevent or reduce environmental pollution by ammonia, so that the negative impact of ammonia pollution can be avoided [4].

One method of removing ammonia that can be done is using the adsorption principle, because the energy adsorption system required is low, easy to operate, and easy to maintain [5]. Some of these methods are very simple and economical, while others are complex and expensive [6].

One of the ideas to reduce ammonia pollution is to take advantage of the high absorption properties of zeolite, which has often been used as an adsorbent for several harmful gases. Ammonia can be absorbed and bound in the pores of the zeolite. Another advantage of using zeolites lies in the weak nature of the bonds of alkaline / alkaline metal ions which can be replaced by ammonium. Ammonium ions that are bound to the surface of the zeolite structure through the calcination process can be converted into H+ ions, which in turn make the zeolite acidic, so that the active zeolite can be used as a catalyst [4].

The activation process of natural zeolite adsorbent can be done physically or chemically [7]. Physical activation is carried out by heating (calcination) which aims to evaporate water trapped in the pores of the zeolite crystals so that the number of pores and specific surface area increases and chemical activation is carried out using a solution of hydrochloric or sulfuric acid which aims to clean the pore surface, remove compounds impurities and rearranging the position of interchangeable atoms [8].

The performance of the fixed-bed column is usually described using a breakthrough curve. However, developing a model to accurately describe the dynamic behavior of adsorption in fixed-bed columns is usually difficult. Therefore, the use of a simple model without a numerical solution is more appropriate and has practical advantages. Some of the most frequently applied models to describe fixed-bed column adsorption are the Thomas model and the Yoon-Nelson model [9].

Thomas's model is known as the bed-depth-service-time (BDST) model [10]. The BDST approach is based on the irreversible isotherm model by Bohart and Adams [11]. This simplified design model ignores the mass transfer resistance between particles (solids) and external resistance (fluid-film) directly. In other words, the adsorption rate is controlled by the surface reaction between the adsorbate and the unused adsorbent capacity. Thomas's equation for the adsorption column is presented in Equation 1[10]:

\[
\frac{C_e}{C_o} = \frac{1}{1 + \exp \left[ \frac{K_{th} (q_o M - C_o V)}{Q} \right]} 
\]

With: Cₐ, Cₒ = solute concentration in effluent and influent (mg / L); qₒ = maximum adsorption capacity (mg / g); M = total mass of adsorbent (g); Q = volumetric flow rate (mL / min); V = throughput volume (mL) and Kₜh = Thomas rate constant (mL / min / mg).

Yoon and Nelson's adsorption kinetics model is based on the assumption that the rate of decrease in the adsorption probability for each adsorbate molecule is proportional to the adsorbate adsorption probability and the adsorbate breakthrough chance on the adsorbent [10]. Yoon and Nelson’s equation regarding a single component system is presented in Equation 2 [10]:

\[
\frac{C_e}{C_o} = \frac{1}{1 + \exp \left[ K_{YN} (r - t) \right]} 
\]

With: Cₐ, Cₒ = solute concentration in effluent and influent (mg / L); KYN = rate constant (1 / min); r = time taken for 50% of the adsorbate breakthrough (men); t = sample breakthrough time (men).

Several parameters are known that affect the performance of the fixed-bed column to adsorb synthetic ammonia. So a series of studies on the absorption of synthetic ammonia by natural zeolite-based adsorbents which are numerous and cheap in Indonesia were conducted. The purpose of this study was to study the effect of variations in bed height on the performance of fixed-bed columns to
adsorb synthetic ammonia using adsorbent from natural zeolite. In addition, the adsorption kinetics were also investigated using the Thomas kinetics model and the Yoon and Nelson model.

2. Research Methodology

2.1 Zeolite preparation
The material used was zeolite Sarulla obtained from North Tapanuli, North Sumatra which was prepared using chemical physics. The raw material is mashed to 100 mesh for absorption in a perfect solution. It was heated at 400 °C for 2 hours to evaporate the water trapped in the zeolite crystal pores, so that the pore number and specific surface area increased. After that, chemical preparation was carried out with a KCl 1.5 M solution for ion exchange (H⁺ or K⁺) from the solution with exchange cations from the zeolite framework. After that it is dried and the dry adsorbent is stored in a tightly closed container ready for use.

Activated adsorbent materials were characterized to determine moisture content, ash content and iodine number. The results of material characterization showed that the water content, ash content and iodine number of the prepared activated carbon were 2.5%; 97.5% and 435.25 mg / g.

2.2 Adsorption study in the fixed-bed column
The fixed-bed column adsorption study was carried out using a glass column with a diameter of 0.5 cm and a height of 110 cm. At the bottom, the column is equipped with a filter paper support to prevent the adsorbent material from being carried away by the outflow. The tank containing the feed water is placed at a higher elevation, so that the water can flow into the column by gravity. The tank is equipped with a valve that functions as a discharge regulator. The water to be treated flows from the feed tank into the column at a rate of 5 and mL / min and is kept constant throughout the experiment. Three types of bed heights (3, 4 and 5 cm or equivalent to 0,5; 0,7 and 0,9 g zeolite) were used in this study. The fixed-bed column adsorption study was carried out for 3 hours. Effluent samples were collected at certain time intervals and analyzed for ammonia content. The experimental diagram is shown in Figure 1.

![Figure 1. Fixed-bed adsorption column apparatus](image-url)
3. Results and Discussions

3.1. Effect of bed height on the breakthrough curve

The effect of bed height for the adsorption of ammonia on the adsorbent at various bed heights (3; 4 and 5 cm), with initial concentrations of ammonia (200 mg / L) at flow rates of 5 and 10 mL / min was investigated in this study. The breakthrough curves for ammonia at flow rates of 5 and 10 mL / min are shown in Figure 2 and Figure 3, respectively.

The results of the study show that the volume of water throughput increases with increasing bed height for both Ammonia. This may imply that an increase in bed height will result in a greater number of sorption sites [12]. Thus, the breakthrough times for both ammonia also increase with increasing bed height. In this study, the value of Ce / C0 ratio for bed height 5 cm was found to be smaller than bed height 3 and 4 cm. This indicated that the bed essentially had not reached saturation at the end of the adsorption operation time of 3 hours.

![Figure 2](image1.png)  
**Figure 2.** Effect of bed height on the breakthrough curve for adsorption of synthetic ammonia with a flow rate of 5 mL / minute on the adsorbent of zeolite

![Figure 3](image2.png)  
**Figure 3.** Effect of bed height on the breakthrough curve for adsorption of synthetic ammonia with a flow rate of 10 mL / min on the adsorbent of zeolite
3.2. Fixed-bed column adsorption kinetics study

To describe the performance of fixed-bed columns and to scale up, the experimental data were further analyzed using the Thomas kinetics model and the Yoon-Nelson kinetics model.

**Thomas's model**

The Thomas model has been used by a number of researchers to investigate adsorption kinetics [13]; [11]. The kinetics coefficient (K_T) and the maximum adsorption capacity (q_o) of the bed were determined by plotting \( \ln \left( \frac{C_0 - C_e}{C_e} \right) \) against time (Figures 4 and 5). The results of the analysis of the KT and q_o values are shown in Table 1.

![Linear plot of synthetic ammonia adsorption experimental data with flow rates of 5 mL / minute (a) and 10 mL / minute (b) with the Thomas model at different bed heights](image)

**Figure 4.** Linear plot of synthetic ammonia adsorption experimental data with flow rates of 5 mL / minute (a) and 10 mL / minute (b) with the Thomas model at different bed heights.
**Figure 5.** Linear plots of synthetic ammonia adsorption experimental data with flow rates of 5 mL / minute (a) and 10 mL / minute (b) Yoon and Nelson models at different bed heights.

**Table 1.** Data of synthesis ammoniac adsorption

| Kinetic Model       | Volumetric Flow Rate mL / minute | 5      | 10     | 5      | 10     | 5      | 10     | 5      | 10     | 5      | 10     | 5      | 10     | 5      | 10     |
|---------------------|----------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
|                     |                                  | 3      | 4      | 5      | 3      | 4      | 5      | 3      | 4      | 5      | 3      | 4      | 5      | 3      | 4      |
| **Thomas**          |                                  |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
| $K_T$ (mL/min/mg)   | 0,023                            | 0,027  | 0,012  | 0,024  | 0,018  | 0,028  |
| $q_0$ (mg/g)        | 279,3589                         | 283,5803 | 324,6593 | 766,0834 | 1,212,8582 | 1,019,69 |
| $R^2$               | 0,551                            | 0,915  | 0,625  | 0,984  | 0,872  | 0,98   |
| **Yoon-Nelson**     |                                  |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
| $K_{YN}$ (L/min)    | 0,008                            | 0,015  | 0,006  | 0,014  | 0,009  | 0,013  |
| $\tau$ (min)       | 27,7711                          | 13,1314 | 15,0968 | 39,5041 | 25,6500 | 35,293 |
| $R^2$               | 0,551                            | 0,915  | 0,625  | 0,984  | 0,872  | 0,98   |
From Table 1 it can be seen that the kinetics coefficient value of KT is influenced by the bed height. In synthetic ammonia adsorption the KT value decreased with increasing bed height. The highest KT value at a flow rate of 5 mL / minute for synthetic ammonia adsorption was 0.012 mL / men / mg at 5 cm bed height, while for bed height 3 and 4 cm the values were smaller, namely 0.023 and 0.027 mL / min / mg, respectively. The maximum adsorption capacity (q0) for synthetic ammonia adsorption values was found to decrease with increasing bed height. Value of q0 for bed height 3; 4 and 5 cm are 279.3589 mg / g, respectively; 283.5803 mg / g and 324.659 mg / g.

In synthetic ammonia adsorption at a flow rate of 10 mL / minute, the kinetics coefficient value of KT was found to increase with increasing bed height. The highest KT value of 0.028 mL / min / mg was found at 5 cm bed height and the lowest KT value of 0.018 at 4 cm bed height. The maximum adsorption capacity (q0) for ammonia adsorption at a flow rate of 10 mL / min was found to increase with increasing bed height. Value of q0 for bed height 3; 4 and 5 cm were 766.0834 mg / g, respectively; 1,212.8582 and 1,019.69 mg / g. The effect of bed height on the KT and q0 values obtained in this study was as reported by Nwabanne and Igbokwe (2012) [11]. The high regression coefficient (R^2) indicates that the kinetics data can be confirmed properly according to the Thomas model.

**Model Yoon and Nelson**

A number of researchers used Yoon and Nelson's model in the study of fixed-bed column adsorption kinetics [12]. The ln [Ce / (C0 - Ce)] plot versus time yields a straight line with the KYN slope and the KYN - intercept (Table 1; and Figures 4 and 5). In synthetic ammonia adsorption, both the value of the KYN rate constants and τ (time required for the effluent concentration to reach 50% of the saturated concentration) decreased with increasing bed height. KYN value for bed height 3; 4 and 5 cm are 0.008 respectively; 0.015 and 0.006 men-1, while the value of τ is 27.7711; 13.1314 and 15.0968 minutes.

In contrast to synthetic ammonia, the value of the KYN rate constant for synthetic ammonia adsorption at a flow rate of 10 mL / min decreases with increasing bed height, while the value of τ increases. KYN value for bed height 3; 4 and 5 cm are 0.014, respectively; 0.009 and 0.013 men-1, while the value of τ is 39.5041; 25.65 and 35.293 minutes. The KYN and τ values which increased with increasing bed height were in accordance with the results reported by Lallan et al. (2017). The high regression coefficient (R^2) indicates that the kinetics data can be confirmed properly according to Yoon and Nelson's model.

**3.3. Ammonia behavior modeling in fixed bed adsorption column**

To predict the adsorption behavior of a component in the adsorption column, a mathematical model is needed [11]. In this study the Thomas Model was selected to fit the experimental data. Figures 6 present experimental breakthrough curves for each adsorbent at a flow rate of 5 mL / min and a bed height of 4 cm.

The calculated theoretical curve according to the proposed model is also shown in Figure 6. It can be seen that the theoretical curve corresponds to the experimental curve. This is in accordance with the results reported by Nwabanne and Igbokwe (2012) and Sivakumar and Palanisamy (2009).
4. Conclusions
The adsorption of ammonia with the adsorbent obtained from zeolite was investigated in a fixed-flow fixed-bed column. The breakthrough curves were determined at various bed heights. To analyze the experimental data and to determine the column characteristics, the Thomas and Yoon-Nelson models were used. These models provide good estimates of experimental behavior. The overall breakthrough curve is well predicted by the Thomas model.

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