INTRODUCTION

Water is a major component in shrimp farming activities. Water will tend to decrease in quality as the water usage continues, while the quality of water used must be maintained (Ariadi et al., 2019). The problems appeared with the limitations of fresh water. The issues connected with water that must be addressed include turbidity, lack of dissolved oxygen, the presence of ammonia (NH₃) and others (Rahman et al., 2015). Failure of harvesting shrimp often experienced by shrimp farmers is one indication of the degradation of land quality and water supporting cultivation efforts, failure occurs as a result of neglect of the carrying capacity or ability of the pond as a medium of cultivation activities (Susetyaningsih et al., 2020).

The shrimp farming technology in general requires a good environment and can meet the physical, chemical, and biological requirements of cultivated commodities. The intensive shrimp cultivation with a high amount of feed has an impact on the increasing cultivation waste derived from leftover feed, feces and shrimp metabolites and when thrown out, it will pollute the environment, including the surrounding cultivation environment. In order to reduce intensive shrimp cultivation waste, technology is needed that can effectively reduce or degrade the remaining feed so that toxic compounds, especially organic materials and some compounds, such as ammonia (NH₃), Nitrite (NO₂), and Hydrogen Sulfide (H₂S), can interfere with the quality of pond water if excessive (Koyama et al., 2020; Farizky et al., 2020). These compounds can be decomposed using zeolite (Aly et al., 2016; Anggoro et al., 2019; Sumantri et al., 2020).

Zeolite is a group of minerals of various chemical compositions with different structures in which zeolites are characterized by porous structures. Zeolite has a special shape that...
produces the ability to selectively absorb ions/particles the size of which does not exceed the diameter of the zeolite pores. In this case, the commercial and environmental use of zeolite is almost unlimited. Zeolite can be applied to absorption (Neolaka et al., 2017; 2018; Kurniawan et al., 2020), ion exchange, and catalyst processes (Hudiyono et al., 2012; Kusuma et al., 2013; Yulizar et al., 2016; Król and Mozgawa, 2019). The adsorption process gained is a promising method for a long-term treatment and economically proven (Ariffin et al., 2017).

Zeolite has adsorption properties that can make it an adsorbent. Zeolite has a high surface area and pores suitable for water (3 Å). In Indonesia, natural zeolite can be found in markets or mining areas. However, the adsorption capacity of natural zeolite is too low, about 0.07–0.09 grams of water per gram of zeolite. In general, natural zeolite contains organic and inorganic receptors, and has a high Si/Al ratio. In addition, the size of the pores is not homogeneous. In order to absorb water, it takes a pore measuring 3 Å that almost equals the diameter of water molecules. Therefore, activation is required before using natural zeolite (Djaeni, et al., 2015).

Indonesia is a country that has a considerable amount of natural zeolite potential and spread in 46 locations, among others in Lampung, West Java, Central Java, and East Java. In terms of the cation exchange capacity (CEC), the quality of Indonesia’s natural zeolite is quite good. However, this huge potential has not been utilized optimally and is only limited to processing industrial waste, supplements on livestock food and fertilizers. Natural zeolite is found, e.g., in the area of South Malang. East Java. The natural zeolite from Malang contains many minerals mordenite type 55–85% and has mordenite crystallinity 38–39%.

In general, the purpose of this study was to produce the water that is safe for shrimp by using zeolite as adsorbent to absorb unwanted substances, especially NH$_3$ and H$_2$S, identify the effect of flow rate on zeolite ability to absorb toxic gases (NH$_3$ and H$_2$S), and determine the rate of absorption (K) and reaction rate (k).

**MATERIALS AND METHODS**

**Materials**

The study used the natural zeolite from Malang (a mountainous city in East Java, Indonesia). By analyzing the BET surface area, it is known that the surface area of the natural zeolite from Malang amounts to 35,599 m$^2$ gram$^{-1}$ with a weight of 3.5 kg. The shrimp pond water used is taken directly from shrimp ponds in the Kendal area (a coastal city of the sea in Central Java, Indonesia) as much as 350 liters.

**Experimental design**

Variable control used shrimp pond water, zeolite weighed 3.5 kg, and the volume of pond water used was 350 L. In turn, the variable used the flow rate are 3, 6, 12 L minutes$^{-1}$ and operating time are 0.24, 48 hours. Observations were made on the concentration of NH$_3$ and H$_2$S at the Initial and End of Shrimp Harvest at each Flow Rate.

The equipment was assembled according to Figure 1, then operated by connecting electricity to the power outlet so that water was pumped into the zeolite, then the sample was tested once every 24 hours. The water purification operations were carried out using a prototype purification tool. The zeolite in the tank of the prototype tool absorbed hazardous substances (H$_2$S and NH$_3$) in the water from the shrimp pond. Then, 3.5 kg of Malang natural zeolite was placed into the adsorbent column. Then, the water purification prototype was turned on for the operating time. The experiment was conducted with the flow rate used (3, 6, 12 L minutes$^{-1}$), Operating time (0, 24, 48 hours), and observations were made by measuring the concentration of NH$_3$ and H$_2$S in pond water.
Kinetic model

In order to obtain the value of $K_D$ or constant of adsorption equilibrium, the following formula has been conducted (Zhang et al., 2017) is

$$K_D = \frac{q_e}{C_e}$$  \hspace{1cm} (1)

where: $K_D$ is adsorption equilibrium constant (L·mol$^{-1}$), $q_e$ is adsorption capacity (mg·gr$^{-1}$), and $C_e$ is concentration at the equilibrium (0.004309 mL·gr$^{-1}$).

For adsorption kinetic model, the kinetic model applied for kinetic model of zero order, first-order, second order, and third order and the formula can be described as are

Zero-order: $C_A = C_{A0} - k_0 t$  \hspace{1cm} (2)

First-order: $-\ln C_A = \ln C_{A0} - k_1 t$  \hspace{1cm} (3)

Second-order: $\frac{1}{C_A} - \frac{1}{C_{A0}} = k_2 t$  \hspace{1cm} (4)

Third-order: $\left(\frac{1}{C_A}\right)^2 = \left(\frac{1}{C_{A0}}\right)^2 + 2 k_3 t$  \hspace{1cm} (5)

where: $C_{A0}$ is initial concentration of $A$ at $t = 0$ (mg·L$^{-1}$), $C_A$ is concentration of $A$ at $t = t$ (mg·L$^{-1}$), $t$ is Time (hour), and $k$ is constant of reaction rate (hour$^{-1}$).

RESULTS AND DISCUSSIONS

Effect of Flow Rate on Zeolites Ability to Absorb Toxic Gases

In this study, an analysis of the initial sample of zeolite of Malang using the help of BET Surface Area Analyzer tool. The analysis of zeolite surface area was conducted in Integrated Laboratory of Diponegoro University, the result of analysis of natural zeolite surface area of Malang is 35.599 m$^2$ gram$^{-1}$. The results of analysis of NH$_3$ and H$_2$S levels can be seen in Figure 2–5:

The zeolite samples were expected to absorb NH$_3$ and H$_2$S contained in the water samples from the shrimp ponds of Kendal area. The treatment used was the difference in flow rate used in the adsorption stage, namely 12, 6, and 3 L·min$^{-1}$ with the same zeolite weight in each variable used by 3.5 kg. The sampling of the shrimp pond water for analysis of the NH$_3$ and H$_2$S levels was carried out every 24 hours until the 48th hour at the beginning of harvest (1st month) and end of harvest (3rd month). The analysis of the NH$_3$ and H$_2$S levels was conducted using the help of Hanna Instrument Ammonia Test Kit, Hach Hydrogen Sulfide test kit, and Protirta Hydrogen Sulfide Strip Test Kit.

From Figure 2–5 and Table 1 and 2, the NH$_3$ and H$_2$S levels were obtained at the beginning of shrimp harvest (1st month) and the end of shrimp harvest (3rd month) which was adapted at flow rate 3, 6, and 12 L·min$^{-1}$. The results indicated that, the zeolite with flow rate of 3L·min$^{-1}$ can absorb the most NH$_3$ and H$_2$S. This is because the flow rate is proportional to time. The smaller the flow rate, the time the water of shrimp ponds makes contact with natural zeolite will be longer, so that the absorption capacity is larger, the greater the surface area of natural zeolite to support H$_2$S and NH$_3$ is.

Effect of Adsorption Equilibrium and Adsorption Kinetics with Flow Rate

The value of adsorption equilibrium constant ($K_D$) can be seen in Table 1 and 2. On the basis of Table 1 and 2, the obtained NH$_3$ adsorption constants at the beginning of harvest and end of harvest in a row for flow rate 3 L·min$^{-1}$ are 11.60362 and 23.20724; for flow rates of 6 L·min$^{-1}$ they are 11.60362 and 23.20724; and for flow rates of 12 L·min$^{-1}$ they are 11.60362 and 11.60362. In turn, for H$_2$S adsorption constants at the beginning of harvest and end of harvest in a flow rate 3 L·min$^{-1}$ are 2.32072407 and 11.60362; for flow rates of 6 L·min$^{-1}$ they are 2.32072407 and 11.60362; and for flow rates of 12 L·min$^{-1}$ they are 11.60362 and 11.60362. In turn, for H$_2$S adsorption constants at the beginning of harvest and end of harvest in a flow rate 3 L·min$^{-1}$ are 2.32072407 and 11.60362; for flow rates of 6 L·min$^{-1}$ they are 2.32072407 and 11.60362; and for flow rates of 12 L·min$^{-1}$ they are 2.32072407 and 4.641448.

On the basis of Table 3 and 4 also obtained kinetic model adsorption of zero order, first order, second order, and third order for adsorption of NH$_3$ and H$_2$S at flow rates of 3, 6, and 12 L·min$^{-1}$.
Figure 2. Effect of flow rate to the adsorption of NH$_3$ at the beginning of harvesting

Figure 3. Effect of flow rate to the adsorption of NH$_3$ at the end of harvesting

Figure 4. Effect of flow rate to the adsorption of H$_2$S at the beginning of harvesting

Figure 5. Effect of flow rate to the adsorption of H$_2$S at the end of harvesting

Table 1. The value of NH$_3$ adsorption constant for each flow rate

| Time                  | Flow rate | t (hour) | K (L·mol$^{-1}$) |
|-----------------------|-----------|----------|------------------|
| Beginning of harvesting (1st month) | 3 L minutes$^{-1}$ | 0 | 0 |
|                       |           | 12       | 11.60362         |
|                       |           | 48       | 11.60362         |
|                       | 6 L minutes$^{-1}$ | 0       | 0 |
|                       |           | 12       | 11.60362         |
|                       |           | 48       | 11.60362         |
|                       | 12 L minutes$^{-1}$ | 0       | 0 |
|                       |           | 12       | 11.60362         |
|                       |           | 48       | 11.60362         |
| End of harvesting (3rd month) | 3 L minutes$^{-1}$ | 0       | 0 |
|                       |           | 12       | 23.20724         |
|                       |           | 48       | 34.81086         |
|                       | 6 L minutes$^{-1}$ | 0       | 0 |
|                       |           | 12       | 11.60362         |
|                       |           | 48       | 23.20724         |
|                       | 12 L minutes$^{-1}$ | 0       | 0 |
|                       |           | 12       | 11.60362         |
|                       |           | 48       | 11.60362         |

Table 2. The value of H$_2$S adsorption constant for each flow rate

| Time                  | Flow rate | t (hour) | K (L·mol$^{-1}$) |
|-----------------------|-----------|----------|------------------|
| Beginning of harvesting (1st month) | 3 L minutes$^{-1}$ | 0 | 0 |
|                       |           | 12       | 2.32072407       |
|                       |           | 48       | 2.32072407       |
|                       | 6 L minutes$^{-1}$ | 0       | 0 |
|                       |           | 12       | 2.32072407       |
|                       |           | 48       | 2.32072407       |
|                       | 12 L minutes$^{-1}$ | 0       | 0 |
|                       |           | 12       | 0               |
|                       |           | 48       | 2.32072407       |
| End of harvesting (3rd month) | 3 L minutes$^{-1}$ | 0       | 0 |
|                       |           | 12       | 9.282896         |
|                       |           | 48       | 11.60362         |
|                       | 6 L minutes$^{-1}$ | 0       | 0 |
|                       |           | 12       | 4.641448         |
|                       |           | 48       | 9.282896         |
|                       | 12 L minutes$^{-1}$ | 0       | 0 |
|                       |           | 12       | 0               |
|                       |           | 48       | 4.641448         |
From the results obtained, based on the best $R^2$ value, the adsorption of NH$_3$ and H$_2$S are satisfied in the first-order kinetic model with $R^2$ of 0.9763 and k value of 0.0007 hours$^{-1}$ in H$_2$S adsorption with a flow rate of 6 L·min$^{-1}$.

From the results obtained, the adsorption constants for NH$_3$ and H$_2$S are best obtained from zeolite weight of 3 L·min$^{-1}$ for filtering 350 L of shrimp pond water. This is because the flow rate is directly proportional to the time. The longer an adsorbent makes contact with adsorbate, the more the effective collision between particles will increase (Botahala, 2019). Adsorption of a dissolved substance will increase when the contact time is longer. Long contact times allow the diffusion and sticking of molecules of adapted dissolved substances to last more. The time to achieve a balanced state in the process of metal absorption by adsorbent ranges from a few minutes to several hours.

### Pond Water Treatment Equipment with Adsorbent Zeolite of Malang

In order to obtain the design of pond water treatment equipment with zeolite adsorbent on a real pond scale, the total required adsorbent needs at the size of shrimp pond scale with adsorption capacity formula ($q_e$) is formulated as follows (Zhang et al., 2017):

$$q_e = \frac{C_0 - C_e}{m} \times V$$  \hspace{1cm} (6)

where: $q_e$ is adsorption capacity (mg·gr$^{-1}$)

$C_0$ is initial concentration (mg·L$^{-1}$)

$C_e$ is concentration at t (mg·L$^{-1}$)

$V$ is adsorbent volume (L)

$M$ is mass of adsorbat (mg)

With an adsorption capacity of 0.15 mg·gr$^{-1}$, an initial NH$_3$ concentration of 1.5 mg·L$^{-1}$, a concentration at 48 hours of 0 mg·L$^{-1}$, and a volume of adsorbat or shrimp pond volume in general of 1,800,000 L, the required adsorbent needs at the shrimp pond scale is 18,000 gr.

| Kinetic model | Parameter | 3 | 6 | 12 |
|---------------|-----------|---|---|----|
| Zero-order    | $R^2$     | 0.5192 | 0.75 | 0.25 |
|               | $k_0$ (hr$^{-1}$) | 0.0007 | 0.0004 | 0.0002 |
| First-order   | $R^2$     | 1·10$^{-2}$ | 0.9297 | 0.25 |
|               | $k_1$ (hr$^{-1}$) | 1·10$^{-2}$ | 0.0005 | 0.0002 |
| Second-order  | $R^2$     | 0 | 1 | 0.25 |
|               | $k_2$ (hr$^{-1}$) | 0.0185 | 0.0006 | 0.0001 |
| Third-order   | $R^2$     | 0 | 1 | 0.25 |
|               | $k_3$ (hr$^{-1}$) | 0.0625 | 0.002 | 0.0005 |

Table 4. Result of linearized of equation model for adsorption kinetic model of H$_2$S

| Kinetic model | Parameter | 3 | 6 | 12 |
|---------------|-----------|---|---|----|
| Zero-order    | $R^2$     | 0.3827 | 0.75 | 0.75 |
|               | $k_0$ (hr$^{-1}$) | 0.0002 | 0.0002 | 9·10$^{-5}$ |
| First-order   | $R^2$     | 0 | 0.9763 | 0.75 |
|               | $k_1$ (hr$^{-1}$) | 0.0224 | 0.0007 | 0.0002 |
| Second-order  | $R^2$     | 0 | 0.9643 | 0.75 |
|               | $k_2$ (hr$^{-1}$) | 0.1111 | 0.0036 | 0.0006 |
| Third-order   | $R^2$     | 0 | 0.9067 | 0.9394 |
|               | $k_3$ (hr$^{-1}$) | 0.1736 | 0.0054 | 0.0006 |
Then, the dimensions of the adsorbent column of the pond scale can be found by comparing with the prototype dimensions of the adsorbent column.

\[
\begin{align*}
d_1 : h_1 &= 0.12 \text{ m} : 0.21 \text{ m} \\
d_2 &= 0.12 \frac{h_2}{0.21} \\
r_2 &= \frac{d_2}{2} \times \frac{h_2}{0.21}
\end{align*}
\]

Hence, the value of \( r_2 \) can be introduced to the formula of adsorbent column volume (volume of tube)

\[
V = \pi (r^2)h
\]

Thus, the dimensions of the farm-scale adsorbent column is tabulated in Table 5.

**CONCLUSION**

The results showed that the adsorption with a flow rate of 3 L·min\(^{-1}\) absorbed more NH\(_3\) and H\(_2\)S compounds compared to the flow rates of 6 and 12 L·min\(^{-1}\). Apart from that, it can be determined that the best adsorption constant (K) has a flow rate of 3 L·min\(^{-1}\). On the basis of the best R\(^2\) values, the adsorption of NH\(_3\) and H\(_2\)S was fulfilled by a first order kinetic model with R\(^2\) of 0.9763 and a k value of 0.0007 hrs\(^{-1}\) in H\(_2\)S adsorption with a flow rate of 6 L·min\(^{-1}\).

From the data above, it can be calculated that the adsorbent needed in the adsorption of NH\(_3\) and H\(_2\)S in a scale shrimp pond amounts to 18 kg of Malang zeolite with a column height of 3.62 m of adsorbent, a diameter of 2.07 m, and a column volume of 12.21 m\(^3\).

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Table 5. Adsorbent dimension column of prototype and shrimp pond scale

| Prototype scale | Volume of pond | Adsorbent column height (h\(_1\)) | Adsorbent column diameter (d\(_1\)) | Radius of adsorbent column (r\(_1\)) | Volume adsorbent column (V\(_1\)) |
|-----------------|---------------|---------------------------------|----------------------------------|-----------------------------------|-------------------------------|
|                 | 350 L (0.35 m\(^3\)) | 0.21 m                          | 0.12 m                           | 0.06 m                           | 2.37 L                        |

| Actual farm scale | Volume of pond | Adsorbent column height (h\(_2\)) | Adsorbent column diameter (d\(_2\)) | Volume of adsorbent column (V\(_2\)) |
|-------------------|---------------|---------------------------------|----------------------------------|-----------------------------------|
|                   | 1800000 L (1800 m\(^3\)) | 3.62 m                          | 2.07 m                           | 12.20 m\(^3\)                    | 12208.32 L                    |
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