Ammonia Removal Using Coconut Shell Based Adsorbent: Effect of Carbonization Duration and Contact Time

Nur Indradewi Oktavitri*, Hery Purnobasuki, Eko Prasetyo Kuncoro, Indah Purnamasari
Department of Biology
Faculty of Science and Technology, Airlangga University, Indonesia
*Corresponding author: nur_i_d_o@yahoo.com

Abstract
The preparation of adsorbent using activated coconut shell was investigated at carbonization duration and adsorption contact time. The coconut shell was activated using physical and chemical activation. This research focused on variation of physical activation such as carbonization. The carbonization had two steps, there are high temperature and medium temperature. This research used 500°C at high temperature and 220°C at medium temperature. The duration of medium temperature was varied in 1, 2, and 4 hours. The chemical activation used H₃PO₄. The ammonia concentration of simulated wastewater around 6000 mg/l. The acclimatization period was 8 d. The coconut shell ability for ammonia removal was observed after acclimatization period in 0, 2, 4, 6, and 8d. The effect of carbonization period and contact time on ammonia adsorption of dairy simulated wastewater was discussed in this research. This research used anaerobic digestion with 10 liter of volume. The concentration of ammonia was measured with nessler methods. Carbonization duration and contact time increased the adsorption capacity. From the obtained result of adsorption isotherm, the Langmuir equation was the best fit for all carbonization period, especially 4-hour carbonization period.

Keywords: activated carbon, adsorption, anaerobic digestion, ammonia removal, carbonization, contact time

I. Introduction
High strength of ammonia is the effluent characteristic of agro/food industry industry [1], [2]. The high ammonia concentration causes stress in environment, therefore the industrial effluent should be managed. Anaerobic digestion is widely used to treat industrial wastewater because of low cost, low sludge production and energy saving [3]. The anaerobic digestion has three main steps process, i.e. acidogenesis, acetogenesis, and methanogenesis. The indicator of successful process of anaerobic digestion is limitation of inhibitor of those processes. High concentration of ammonia, heavy metal, unstable pH are problems of anaerobic process [4], [5]. The fail of the process is usually caused by the existence of high value of ammonia.

Ammonia is produced from wastewater and it is resulted from degradation of organic substance from anaerobic process [6]. Therefore, the ammonia concentration increases potentially during anaerobic process. The parameter indicates the amount of ammonia is Total Ammonia Nitrogen. The total Ammonia Nitrogen consist of ammonium ion and free ammonia. The ammonium ion interacts with membrane cell of microorganism [4]. It causes decreasing of microorganism population. Methanogene bacteria is the genus of bacteria intolerant with high ammonia concentration.

There are many ammonia removal technologies, such as chemical precipitation, air stripping, nitrification, and denitrification, anaerobic ammonium oxidation, short-cut nitrification and combination of those process [7]. However, those processes require complex process and expensive operation and maintenance. The adsorption is effective methods for removal ammonia [8]. There are several kind of adsorbents, such as activated carbon coconut shell [8]; clay [9], and zeolite [10]–[12]. Activated carbon is recommended by [13] to adsorb pollutant. In order to make competitive adsorbent, activated carbon from nature such as coconut shell is suggested by Boopathy et al [8].
In order to enhance the adsorption capability of adsorbent, the activation process is recommended for it [14], [15]. The physic activation with high temperature influences the pores characteristic of adsorbent [16]. In addition, Legrauri et al [17] informed that variation of activated time in high temperature give different response of adsorbent to remove pollutant. In addition, the ability of adsorbent gives real performance in several contact time.

This research aims to evaluate the adsorption capacity of activated carbon from coconut shell with variation of carbonization periods. The result of the experiment is fitted to the adsorption capacity of activated coconut shell using Freundlich and Langmuir as famous isotherm model. Isotherm model is used to evaluate adsorption capacity of ammonia using activated coconut shell, Therefore, the model can be applied in industry scale [18].

II. Materials and Methods

2.1 Preparation of Adsorbent from Activated coconut shell

This research used fine powder of coconut shell char to got optimized adsorption process from the Coconut shell char [19]. The coconut shell char was activated using physical and chemical activation. The activation process enhanced the ability of coconut shell char to adsorb the contaminant [15]. Before the activation step, the fine coconut shell char was rinse using tap water. At physical activation step (carbonization periods), coconut shell char was dried at 220°C using oven (Memmert series 100-800) [8]. The activation process enhanced surface area of activated coconut shell [20]. The variable for carbonization period used were 1, 2, and 4 hours in 220°C. The activated coconut shell was contacted with H3PO4 10% for chemical activation.

2.2 Dairy simulated waste water

This research used dairy simulated wastewater. Dairy simulated wastewater consists of NH4Cl, 1 g KH2PO4; 0,05 MgSO4.7H2O; 0,038 g CaCl2; 2 g NaHCO3 for 1 litre of simulated waste water [21]. The ammonia concentration of dairy simulated wastewater was 6000 mg/l. The substrate feed as inoculums for anaerobic process was collected from Pegirian Slaughter House, Surabaya, Indonesia. The substrate was added to wastewater was 1/100 (v/v).

2.3 Design of reactor

Three batch reactors from Low Density Polyethylene (LDPE) were operated in this research for 15 days. Total volume of reactor was 12 L. The 10 L simulated waste water was added to the reactor and total activated coconut shell was added 200 g. The sampling port at 13 cm of height reactor. The illustration of reactor was figured out at Figure 1. The performance of every reactor was measured using Total Ammonia Nitrogen (TAN). The monitoring of adsorption process will be held in 8 d after acclimation. The acclimation need 8 d. The reactors were monitored every 2 days.

2.4 Analytical methods
Total Ammonia Nitrogen (TAN) with nessler methods was analysis based on Standard Methods [22].

III. Results and Discussion

3.1. Effect of Carbonization Period

The carbonization step was part of activation process. The activation step increased the pore size of media. Boopathy et al [8] informed that the pore size after 1-hour activation reached 20 μm. The effect of carbonization duration to adsorption capacity was appeared in Figure 2. The equation to measured adsorption capacity using Equation (1). The increasing of carbonization period enhanced the adsorption capacity. It possibly caused by long duration of carbonization enhanced the pores size of coconut shell.

\[ q_e = \frac{(C_o - C_t)v}{m} \]  

(1)

Where:

Co, Ce, qe as TAN concentration at t=0; as TAN concentration after adsorption process; as adsorption capacity at equilibrium, respectively.

![Figure 2 Effect of carbonization duration to adsorption capacity](image)

3.2. Effect of Contact Time

The effect of contact time on adsorption capacity was described in figure 3. The adsorbent was carbonized in 220°C for 1 hour and contacted with simulated wastewater for 2, 4, 6, and 8 days. In The adsorption capacity of ammonium (qe) increased significantly in 8 days observation. It indicated that the Coconut shell sites unsaturated after 8 days observation and potentially adsorbed ammonia more than 8 days. The research of Kučič [23] presented that the adsorbent saturated in certain time if the qe line in graph in stationer position.

![Figure 3 Effect of contact time on adsorption capacity](image)
3.3 Adsorption Isotherm

The adsorption process described with adsorption isotherms [24]. The capability of adsorbent for removing pollutant under certain condition was provided with isotherm equation. The amount of exchanged ion by coconut shell when equilibrium concentration was described in ion-exchange isotherm [25]. The Freundlich and Langmuir models were used to evaluated adsorption model of ammonia in several contact time. The freundlich equation was described in Equation (2).

\[ q_e = K_F \cdot C_e^{\frac{1}{n}} \]  

Where: \( K_F \) (as Freundlich indicator of adsorption capacity) and \( \frac{1}{n} \) (is the adsorption intensity). The logarithmic form of Freundlich Equation (3) [10], [23].

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  

where values of \( K_F \) and \( n \) are calculated from the intercept and slope of the plot.

Figure 3. Effect of contact time to adsorption capacity

Figure 4 described linear regression equation of Freundlich Isotherm which \( y \) was \( \log q_e \), logarithmic of adsorption capacity from each activation time. The different equation implicated to difference slope and intercept of those equation. It was caused by different treatment for adsorbant [26]. The slope from linear regression, \( 1/n \) value, indicated of the favorability of adsorption. \( n \) values from three different activation time was \( n < 1 \) (Table 1). The \( 1/n \) value around 0.1 and 0.5 easily to adsorb; and more than 2 is hard to adsorb [12]. The experimental results indicated that complexity of wastewater simulation characteristic made activated coconut shell unfavorable to adsorb ammonia. The \( R^2 \) of coconut shell with 4-hour activation closest to 1 indicated that it more suitable to Freundlich Isotherm than 1 and 2 hours activation.

The Langmuir equation was another famous isotherm model. The difference between Freundlich and Langmuir were assumption of adsorption layer. The Langmuir theory assumed monolayer coverage of adsorbate over a homogenous adsorbent surface [23]. A basic assumption is that all adsorption sites are equivalent and adsorption on active sites is independent of whether the adjacent is occupied [12]. The Langmuir equation in Equation (4) and (5) [27].
And linear equation was:

\[ \frac{C_e}{q_e} = \frac{1}{bK_L} + \frac{1}{b}C_e \]  

(5)

Where \( K_L \) is the Langmuir adsorption constant related to the energy of adsorption (l/mg) and \( b \) is the mono-layer adsorption capacity of adsorbent (mg NH4+-N/g). Therefore, a plot of \( \gamma_e/q_e \) versus \( \gamma_e \) gives a straight line of slope \( 1/b \) and intercept \( 1/(b \cdot K_L) \) (Figure 5).

The values of \( K_F, K_L, n, b \) and \( R^2 \) for different activation time of coconut shell, are given in Table 1. Figure 5 also indicated that different equation and \( R^2 \) for different activation time. It also indicated that 1-hour activation was the best fit equation with \( R^2 \) closest to 1 (Table 1). It was suitable with Langmuir equation.

Figure 5 Linear Equation of Langmuir Isotherm with Different Activation Time

Table 1 The values of \( K_F, K_L, n, b \) and \( R^2 \)

<table>
<thead>
<tr>
<th>Isotherm Equation</th>
<th>Component</th>
<th>M1-6000</th>
<th>M2-6000</th>
<th>M4-6000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich Isotherm</td>
<td>Slope (1/n):</td>
<td>0,146</td>
<td>0,233</td>
<td>0,251</td>
</tr>
<tr>
<td></td>
<td>( n ):</td>
<td>6,84932</td>
<td>4,29184594</td>
<td>3,98406</td>
</tr>
<tr>
<td></td>
<td>Intercept (log ( K_F )):</td>
<td>1,25</td>
<td>0,961</td>
<td>0,823</td>
</tr>
</tbody>
</table>
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\[
\begin{align*}
K_L &: 17,7828 \\
R^2 &: 0,844 \\
\text{Langmuir Isotherm} &
\begin{align*}
M1-6000 &
\begin{align*}
\text{Slope (1/b)} &: -54,77 \\
b &: -0,0183 \\
\text{Intercept (1/b.K}_L&) : &268,5 \\
\text{R}^2 &: 0,765 \\
M2-6000 &
\begin{align*}
\text{Slope (1/b)} &: -119,6 \\
b &: -0,0083612 \\
\text{Intercept (1/b.K}_L&) : &482,9 \\
\text{R}^2 &: 0,702 \\
M4-6000 &
\begin{align*}
\text{Slope (1/b)} &: -126,9 \\
b &: -0,0079 \\
\text{Intercept (1/b.K}_L&) : &545,4 \\
\text{R}^2 &: 0,967
\end{align*}
\end{align*}
\end{align*}
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Acknowledgment
This research is part of research grant which sponsored by DIPA Ditlitabmas 2015 Number: 519/UN3/2015, 26 March 2015.

Reference


