Degradation of NH\textsubscript{3} and BOD in Domestic Wastewater using Algal-bacterial System

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Abstract: The objectives of this research were to: 1. Determine the characteristics of Kalidami Boezem water in Surabaya, Indonesia. 2. Examine the level of NH\textsubscript{3} and BOD content in boezem water. The research was conducted with two repetitions with varied addition of KH\textsubscript{2}PO\textsubscript{4} and carbon. The addition of KH\textsubscript{2}PO\textsubscript{4} concentration was adjusted to 0\%, 1\%, and 3\%. Source of carbon (C) used was sucrose 0 mg/L and 29.4 mg/L. The reactor used was glass reactor with volume of 8 L. A total of 12 reactors were performed during the 18-day study. The results showed that the characterization of boezem water of Kalidami, Surabaya has pH value of 7.46, temperature value of 33.00 °C, total P concentration of 1.43 mg/L, NH\textsubscript{3}-N concentration of 10.80 mg/L, COD concentration of 122.30 mg/L, and BOD concentration of 52.60 mg/L. The highest NH\textsubscript{3}-N concentration decreasing efficiency occurs in the reactor with the addition of K element of 0\% and C 29.40 mg/L of 97.92% on day 18, with the final NH\textsubscript{3}-N concentration was 0.23 mg/L. The highest BOD concentration decreasing efficiency occurs in the reactor with the addition of K element of 1\% and C 29.40 mg/L of 61.03% on day 18, with the final BOD concentration was 20.50 mg/L.

1 INTRODUCTION

Domestic wastewater in the city of Surabaya is usually directly discharged into the water bodies, one of which is Kalidami Boezem, Surabaya. Water bodies consisting of rich organic matter and nutrients will create eutrophic conditions. This condition is a toxic contaminant for most aquatic biotas. Therefore, the applicable waste water treatment is needed to reduce organic matter and nutrient in Kalidami Boezem, Surabaya.

High Rate Algal Reactor (HRAR) is adopted from High Rate Algal Pond (HRAP), which is widely used in domestic wastewater treatment to decompose organic matter and nutrient in domestic wastewater (Assemany et al., 2015). HRAR reduces organic matter and nutrient by producing oxygen from algal photosynthesis which is used by bacteria to decompose organic matter and nutrient. HRAR combines the simplicity of the method, economical costs, and the ability to reduce organic matter through oxygen production from the photosynthetic process of algae. The principle of HRAR operations is the use of wastewater as a nutrient source for algal growth, then algae produce oxygen for bacteria to break down substances organic and to perfect this symbiotic cycle, algae use CO\textsubscript{2} produced by bacteria for photosynthesis (Pasaribu et al., 2018). The result of this biological treatment is a decrease in organic matter and nutrient levels. The source of O\textsubscript{2} used in HRAP naturally includes photosynthesis from algae and absorption of oxygen from the atmosphere.

The concept of HRAP was discovered by Oswald and colleagues in the mid-fifties (Oswald et al., 1957) and this system has been used in various countries throughout the world. HRAP in wastewater treatment and nutrient recycling is based on symbiotic interactions between heterotrophic bacteria and algal cells live in a pond as explained by Subagiyono et al. (2015). Biological reactions that appear on the algae pond reduce the organic content and nutrients in wastewater by the help of bacteria and by changing nutrients into algal biomass through photosynthesis. Simatupang et al. (2017) have reported that factors affecting the performance of HRAP and the production of algae is the availability of carbon (C) and nutrient sources, temperature, light intensity, mixing or turbulence, the depth of the pond, and hydraulic retention time (HRT).
Ratnawati et al. (2017) have reported that the efficiency of decreasing BOD and COD levels in boezem water using HRAP was 52.09% and 50.94%, respectively. Boezem water bioremediation can reduce NH₃ 98% and BOD 52% (Nurhayati, 2019). Processing of sago wastewater with symbiosis of bacterial algae can reduce COD 90.29%, BOD 82.74%, TSS 84.52%, nitrate 82.85% and phosphate 98.66% (Pasaribu, 2018). The objectives of this research were to: 1. Determine the characteristics of Kalidami Boezem water in Surabaya, Indonesia. 2. Examine the level of NH₃ and BOD content in boezem water using HRAR.

2 MATERIALS AND METHODS

2.1 Domestic wastewater

Domestic wastewater was taken from Kalidami Boezem, which was located in Kalisari Damen Street, Mulyorejo, Surabaya, Indonesia. The characterization of domestic wastewater measured are shown in Table 1.

Table 1: Characterization of Kalidami’s domestic wastewater

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameters</th>
<th>Unit</th>
<th>Quality standard</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH value</td>
<td>-</td>
<td>6-9</td>
<td>7.46</td>
</tr>
<tr>
<td>2</td>
<td>Temperature</td>
<td>°C</td>
<td>Deviation</td>
<td>33.00</td>
</tr>
<tr>
<td>3</td>
<td>Total P</td>
<td>mg/L</td>
<td>1</td>
<td>1.43</td>
</tr>
<tr>
<td>4</td>
<td>NH₃-N</td>
<td>mg/L</td>
<td>(-)</td>
<td>10.80</td>
</tr>
<tr>
<td>5</td>
<td>COD</td>
<td>mg/L</td>
<td>50</td>
<td>122.30</td>
</tr>
<tr>
<td>6</td>
<td>BOD</td>
<td>mg/L</td>
<td>6</td>
<td>52.60</td>
</tr>
</tbody>
</table>

*Provincial Regulation of East Java No. 2, 2008 (-): not required

2.2 Algae culture

Algae were taken from fresh water ponds in the Wonorejo area, Surabaya, Indonesia. The initial chlorophyll a of algae culture that is ready to be used for research was with a minimum of 3.5±0.5 mg/L (Ratnawati et al., 2017). The chlorophyll a was analyzed using spectrophotometric method (Eaton, Clesceri, and Greenberg, 2005).

2.3 Range Finding Test (RFT)

The aim of RFT was to determine the volume ratio of domestic wastewater and algae culture that can still be tolerated by algae. The volume ratio (%/%) of composition of domestic wastewater and algae culture used in RFT was 25:75, 50:50, and 75:25. RFT was tested by using glass reactor with the volume of 2 L for 7 days.

Chlorophyll a concentration during RFT in the ratio of domestic wastewater and algae culture was 25:75, 50:50, and 75:25 i.e.: 3.8 mg/L, 2.6 mg/L, and 1.3 mg/L, respectively. RFT was done until chlorophyll a concentration with a minimum of 3.5 mg/L was obtained (Ratnawati et al., 2017). The ratio of domestic wastewater and alga culture was 25:75 and was used for the HRAR with concentration of chlorophyll a amounted to 3.8 mg/L.

2.4 High Rate Algal Reactor (HRAR)

Twelve experimental conditions were tested in duplicate during 18 days using laboratory-scale reactors (Table 2). The experimental design comprised three additional doses of potassium (K) elements (0%, 1%, and 3%) and two additional doses of carbon (C) elements which were sucrose (0 mg/L and 29.4 mg/L).

Table 2: Experiment condition

<table>
<thead>
<tr>
<th>Reactor</th>
<th>KH₂PO₄ concentration (%)</th>
<th>Sucrose (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% K</td>
<td>0</td>
<td>29.4</td>
</tr>
<tr>
<td>0% K, C</td>
<td>0</td>
<td>29.4</td>
</tr>
<tr>
<td>1% K</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>1% K, C</td>
<td>1</td>
<td>29.4</td>
</tr>
<tr>
<td>3% K</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>3% K, C</td>
<td>3</td>
<td>29.4</td>
</tr>
</tbody>
</table>

Glass reactors of 4 L volume capacity were prepared for this research. About 3 L domestic wastewater and algae culture was placed in these reactors. The sample from each reactor was collected on days 0, 3, 6, 9, 11, 13, 16, 18. The parameters measured were NH₃-N concentration and BOD. The sample was analysed in accordance with the Indonesia National Standard. The analysis of NH₃-N concentration and BOD was with SNI 06-6989.30-2005 (Indonesia National Standard, 2005) and SNI 06-6989.72-2009 (Indonesia National Standard, 2009), respectively.
3 RESULTS AND DISCUSSION

3.1 NH₃-N concentration

NH₃-N concentration during the research are shown in Figure 1. Initial NH₃-N concentration of all treatments was 10.80 mg/L, and decreased until the end of research. Figure 1a shows that the variation trends of NH₃-N concentration in reactor without addition K (0%K) and reactor without addition K and with addition C (0%K, C) were approximately similar. At the beginning of day 3 of the research, NH₃-N concentration sharply declined with NH₃-N concentration in (0%K) and (0%K, C) was 1.81 mg/L and 2.42 mg/L, respectively. The NH₃-N concentration gradually decreased until the end of the research with the final NH₃-N concentration was 0.53 mg/L (0%K) and 0.23 mg/L (0%K, C). The efficiency of decreasing NH₃-N concentration with addition of C was higher than without addition of C, which was 95.14% (0%K) and 97.92% (0%K, C).

The NH₃-N concentrations decreased because of the nitrification process. NH₄⁺ is converted to NO₂⁻ by *Nitrosomonas*. NO₂⁻ is further converted to NO₃⁻ by *Nitrobacter* (Assemany et al., 2015; Ratnawati et al., 2016) with the equations:

\[
\text{NH}_4^+ + \frac{3}{2} \text{O}_2 \rightarrow \text{NO}_2^- + \text{H}_2\text{O} + 2 \text{H}^+ \quad (1)
\]

\[
\text{NO}_2^- + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_3^- \quad (2)
\]

The NH₃-N concentrations decreased because of the decomposition process and absorption of organic materials by bacteria (Ratnawati and Talarima, 2017). Nurhayati et al. (2017) have reported the algal-bacterial symbiosis in biodegradation of organic materials of boezem water. Heterotrophic bacteria in metabolic process degrade organic materials into inorganic materials which are absorbed by algae during photosynthesis. The results of photosynthesis are in the form of water (H₂O), oxygen (O₂), and energy. Oxygen, which is the result of photosynthesis, is used by bacteria to decompose organic materials in boezem water (Pasaribu et al., 2018). Algae growth increases along with increasing inorganic compounds that are used as nutrient for algae so that NH₃-N is decreasing. Algae use NH₃-N concentration as the main source of N to build the cell protein material by photosynthesis reaction (Ratnawati and Al Kholif, 2018).

Figure 1b and 1c also have the variation trends for NH₃ concentration that were approximately similar. The NH₃ concentration sharply declined on the day 3 of the research, then gradually decreased until the end of the research. Figure 1b shows that in reactor with addition K 1%, NH₃-N concentration in day 3 was 3.28 mg/L (1%K) and 3.13 mg/L (1%K, C). The final NH₃-N concentration in reactor without addition of C (1%K) was higher than it was in reactor with addition of C (1%K, C), that were 2.16 mg/L and 0.97 mg/L, respectively. The efficiency decreased NH₃-N concentration was 80% (1%K) and 91.02% (1%K, C).

Figure 1c shows NH₃-N concentration in day 3 of the research. In reactors with addition of K 3%, without C (3%K) and with C (3%K, C), NH₃-N concentration was 5.86 mg/L and 4.26 mg/L. The final NH₃-N concentration in both reactors had the same concentration, that was 3.57 mg/L. The efficiency of decreased NH₃-N concentration in both reactors was 66.94%.

![Graph](image1.png)

(a) Initial concentration

![Graph](image2.png)

(b) Final concentration
From this study, it can be seen that the K elements addition did not have an effect on the decrease of NH$_3$-N concentration, but the C elements addition has an effect on decreasing NH$_3$-N concentration through little differences. This happened because in reactor, the nutrients and O$_2$ for the growth of algal-bacterial symbiosis are sufficient; so the process of organic materials decomposition in the boezem water is optimal (Nurhayati et al., 2017). Subagiyto et al. (2015) have reported that the KH$_2$PO$_4$ and K$_2$HPO$_4$ addition functions as buffer, namely the pH controller affecting bacterial cell density. The addition of carbon source (sucrose) is as food source and bacterial energy (Ratnawati and Al Kholfi, 2018).

### 3.2 BOD concentration

Initial BOD concentration in all reactors was 52.60 mg/L (Figure 2). BOD concentrations tended to decrease in the first 13 days of the research, then slightly increased until the end of the research. Figure 2a shows the first 3 days of the research. BOD concentration sharply declined to 30.70 mg/L (0%K) and 25.50 mg/L (0%K, C). BOD concentration slightly decreased until the first 13 days of the research and fluctuated until the end of research. The final BOD concentration in (0%K) and (0%K, C) reactor was 29.60 mg/L and 24.70 mg/L, respectively. The efficiency decreased BOD concentration was 43.73% (0%K) and 53.04% (0%K, C).

BOD concentration decreased because it was degraded by bacteria. Organic materials in the form of BOD concentration are used as nutrient and food source for bacterial growth, so there is a reduction in BOD concentration. Biological reactions of bacteria will decompose organic compounds into simple compounds, inorganic products, and energy production for bacteria. The decomposition process is shown in the reaction below (Metcalf and Eddy, 2004):

\[
\text{(COHNS)} + \text{O}_2 + \text{aerobic bacteria} \rightarrow \text{CO}_2 + \text{NH}_3 + \text{product} + \text{energy} 
\]

(3)

Synthesis or assimilation process:

\[
\text{(COHNS)} + \text{O}_2 + \text{aerobic bacteria} + \text{energy} \rightarrow \text{C}_4\text{H}_2\text{O}_2\text{N} (\text{new bacterial cell}) 
\]

(4)

C$_4$H$_2$O$_2$N is a chemical formula used to represent bacterial cells. Lack of organic levels will push bacteria to undergo endogenous respiration, or commonly called as selfoxidation, using its own tissue as a substrate.

\[
\text{C}_4\text{H}_2\text{O}_2\text{N} + 5 \text{O}_2 \rightarrow 5 \text{CO}_2 + \text{NH}_3 + 2 \text{H}_2\text{O} + \text{energy} \]

(5)

The compounds CO$_2$ and NH$_3$ are nutrients for algae. With sufficient sunlight, then algae photosynthesis will occur:

\[
\text{NH}_3 + 7.62 \text{CO}_2 + 2.53 \text{H}_2\text{O} \rightarrow \text{C}_{7.62}\text{H}_{6.06}\text{N} (\text{new algal cell}) + 7.62 \text{O}_2 
\]

(6)

In natural conditions where water receives a little organic matter, the oxygen produced in equation 6 can be used by bacteria in equations 3 and 4 and the cycle is repeated. This cycle, called "algae-bacterial symbiosi" is a natural phenomenon that occurs in water body that receives low organic loading and symbiotic reactions of these algae are in state of dynamic equilibrium.

The reduction in BOD concentration in the reactor happens because of the algal-bacterial symbiosis. Alga will produce O$_2$ in photosynthesis. Bacteria will use O$_2$ for its life and degrade organic materials into CO$_2$. Then CO$_2$ is used by alga for photosynthesis (Simatupang et al., 2017). Metabolic process in heterotrophic bacteria degrades organic materials in boezem water, then algae use it for photosynthesis and process them into H$_2$O, O$_2$, and energy (Pasaribu et al., 2018). Nurhayati et al. (2017) have reported that BOD concentration decreases because of adequate nutrients requirements for the growth of algal-bacterial symbiosis.

There are similar patterns in Figure 2a and Figure 2b. In Figure 2b (reactor with the addition K 1%), BOD concentration decreased in 3 days of the research until 13 days of the research, then it increased at the end of the research. The final BOD concentration was 28.10 mg/L (1%K) and 20.50 mg/L (1%K,C). The efficiency decreased BOD concentration were 46.58% (1%K) and 61.03% (1%K,C).
BOD concentration decreased in the first 13 days of the research, then slightly increased until the end of the research (Figure 2c). The final BOD concentration in (3%K) and (3%K, C) was 29.40 mg/L and 26.80 mg/L, respectively. The efficiency decreased BOD concentration in (3%K) and (3%K, C) was 44.11% and 49.50%, respectively.

The highest reduction of BOD concentration occurred in the reactor with the addition of 0% K element and 29.40 mg/L C source (0%K, C) on day 13, with an efficiency BOD decreased by 53.04% and the final BOD concentration was 24.70 mg/L. The addition of K element did not have an effect on decreasing BOD concentration, but the C element had an effect on decreasing BOD concentration. This occurred because the growth of algal-bacterial symbiosis in the reactor met their nutritional needs. The nutrients needed by bacteria for growth are C, N, S, P, Ca, Zn, Na, K, Cu, Mn, Mg, vitamins, water, and energy (Annisah, 2015). Addition of sucrose as element of C serves as an energy source that can increase bacterial growth so that the BOD concentration can decrease. K element, as a macro nutrient that functions to change the physical form of molecular enzymes, exposes active chemical sites that are suitable for reactions. K element also neutralizes various organic anions and other compounds in plants, which help stabilize pH between 7 and 8, which is optimal for most enzyme reactions. K element also plays a major role in the transportation of water and nutrients in the xylem of all plants.

Fallowfield et al. (2010) have reported that a decrease in BOD reached 95% and COD reduction reached 85% in the study using an algae pond integrated with facultative ponds and sedimentation ponds, which were placed after the algae pond. Lim et al. (2010) used Chlorella vulgaris and Eichhornia crassipes on HRAP to process waste from the rubber industry and obtained 92.9% decrease in COD. Whereas, research conducted by Lim et al. (2010) using Chlorella vulgaris, with 10% of the amount is algae inoculum, to remediate textile waste has mentioned that the decrease obtained from pond was 62.27%. Microbes grow on nutrient media containing compounds certain organic chemistry as the only source of carbon and energy or as the only source of nitrogen.

4 CONCLUSIONS

The characterization boezem water of Kalidami, Surabaya, has pH value of 7.46, temperature value of 33.00°C, total P concentration of 1.43 mg/L, NH3-N concentration of 10.80 mg/L, COD concentration of 122.30 mg/L, and BOD concentration of 52.60 mg/L. The highest NH3-N concentration decreasing efficiency occurred in the reactor with the addition of K element 0% and C 29.40 mg/L on day 18, which was 97.92%, with the final NH3-N concentration was 0.23 mg/L. The highest BOD concentration decreasing efficiency occurred in the reactor with the addition of K element 1% and C 29.40 mg/L on day 18, which showed the percentage of 61.03%, with the final BOD concentration of 20.50 mg/L. The addition of K element did not have an effect on NH3-N and BOD concentration decreased, but the C element had an effect on NH3-N and BOD concentration decreased.
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