SELF-PURIFICATION PERFORMANCE OF BRANTAS RIVER IN EAST JAVA FROM AMMONIA DEOXYGENATION RATE

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ABSTRACT

Naturally the river has the ability to recover from pollutants. The ability of river self recovery is a complex process from the dynamics of dissolved oxygen (DO). DO concentrations in river are influenced by atmospheric reaeration processes, respiration and photosynthesis of algae, oxidation of organic carbon, nitrogen and SOD. Nitrogen oxidation is known as the nitrification process which consists of oxidation of Ammonia in the beginning and subsequent Nitrite oxidation. Both of these nitrification processes have two-way reactions that produce hydroxyl ions. The more hydroxyl ions will shift the equilibrium of the reaction to the left, which causes the formation of higher ammonia. In an effort to control river pollution with mathematical modeling, information on river deoxygenation values is needed, one of which is the ammonia oxidation process. During this time the value of ammonia deoxygenation was taken from other studies and literature which took a long time in the model calibration process. The calibration process will be faster when using the primary data of modeled river. So the purpose of this study is to determine the rate of ammonia deoxygenation. The method of determining the Ammonia deoxygenation rate using the Thomas method is a statistical method using long-term Ammonia analysis data for 1 - 30 days with a time interval of 1, 2, 3, 4, 5, 15, 20, 25, 30 days. Determination of the sampling point using the monitoring point of Jasa Tirta I Company as the manager of the Brantas river. River water quality sampling using the SNI 6989.57: 2008 method Sampling Method of Surface Water. Ammonia analysis uses spectrophotometric method. The results showed that the content of the Brantas Ammonia in the range 0 - 0.278 mg / L. While the results of determining the Ammonia deoxygenation rate ranged from 0.034 to 0.120 / day. This Brantas river deoxygenation level shows the performance of the ammonia oxidation process carried out by AOA and AOB. From the value of the Ammonia deoxygenation rate, it is known that the Brantas river from upstream to downstream has self-purification from Ammonia pollutants.

Key words: ammonia, deoksigenation rate, BOD, Thomas method, self purification.

1. INTRODUCTION

Rivers naturally have the ability to recover from pollutant. This ability determines the sustainability of the river as a natural resource (Dewata, 2018). The preservation of the river provides maximum carrying capacity for the welfare of human life (Dou, et al., 2015; Wang, 2015). The ability to recover from pollutants is known as self purification. So that in the effort to conserve the river, research on self-purification continues to develop in the world.

The ability to recover the river is determined by the availability of dissolved oxygen. Kinetics of river dissolved oxygen are very important in the river's self-recovery ability. The oxygen kinetics dissolved by the river is a complex system of reaeration, photosynthesis and algae respiration, carbon oxidation (Ludang and Mangkoedihardjo, 2009; Mangkoedihardjo, 2007), nitrification and SOD proceses (Palmer, 2001).

One process in the river dissolved oxygen kinetics is Ammonia oxidation which is an aerobic reaction. Nitrobacter bacteria use oxygen to decompose ammonia to nitrite. The level of reduction of dissolved oxygen for the Ammonia oxidation process was the goal in this study.

Ammonia deoxygenation value is needed in modeling river water quality. The river quality model is an approach in river quality management to design management scenarios based on historical conditions. Deoxygenation value River carbon will speed up the model calibration process (Haider, 2010). The use of secondary data on Ammonia deoxygenation level requires time in the model calibration trial error process.
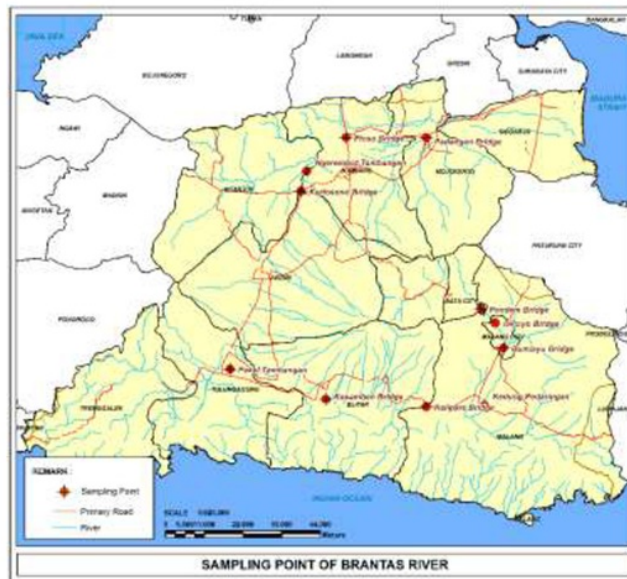
Figure 1 Sampling Point

In this research, Thomas method used to determine the level of Ammonium deoxygenation. Several methods of determining value of the rate of deoxygenation have been used like a method Moment, Least Square, Thomson, Iteration, Fujimoto (Singh, 2007). Besides, also used of the methods O'Connor's (Roquibul, 2006) and Streeter Phelps formula (Singh, 2007) From some of these methods, the non-linear regresion method, Least Square and Thomas should be the first choice in parameter estimation BOD (Oke, 2005). This research was carried out on the Brantas river in East Java Indonesia with a division of 10 segments. Upstream of the river at the sampling location of the Batu City Pendem Bridge. While downstream of the river in the Mojokerto Padangan Bridge as shown in figure 1. River water sampling is carried out in April 2018 during the dry season.

2. MATERIALS AND METHODS

Sampling river water based on SNI 6989.57 : 2008 Sampling Method of Surface Water (SNI, 2008). Analysis of Ammonia for each sample using spectrophotometric method (Liang, 2016). Determination of value of deoxygenation rate of Ammonia or K_{NH} using the method of Thomas with the following formula .

$$(t/y)^{1/3} = 1/(2,3K_{NH}NH_0)^{1/3} + \left[(2,3K_{NH})^{2/3}/6NH_0^{1/3}\right]t \qquad (1)$$

Plot $(t/y)^{1/3}$ with t result slope as $(2,3K_{NH})^{2/3}/6NH_0^{1/3}$ and intercept as $1/(2,3K_{NH}NH_0)^{1/3}$. Deoxygenation value, K_{NH} and NH_0, calculated using this following formula.

$$K_{NH} = 2,61(slope/intercept) \qquad (2)$$

$$NH_u = 1/(2,3\ K_{NH}.intercept^3) \qquad (3)$$

Thomas method is a graphical analysis based on mathematical function equations. The differential method of logarithms was developed by the Fair in 1936. This method is based on a mathematical ratio. BOD observation is required at the same time interval based on the selection of 2 (two) BOD data points at 2t and t. From here the two points of BOD and BOD separation rates can be calculated. Non-linear regression method, least squares or Thomas should be the first choice in the BOD parameter estimation. Although it can be argued that non-linear codes are harder to implement, advanced computer use and the existence of computer packages or routine estimation of non-linear parameters will be easier implementation (Oke, 2005). In determining the deoxygenation rate, long-term Ammonia data are used with Ammonia analysis time intervals in 1, 2, 3, 4, 5, 10, 15, 20, 25 and 30 days.

3. RESULTS AND DISCUSSION

### 3.1. Analysis Result of Long Term Ammonia

Ammonia analysis done by taking a long-term Ammonia analysis with time interval 1 day , 2 days , 3 days , 4 days , 5 days , 10 days , 15 days , 25 days , and 30 days . Conducted sampling at any monitoring points at the river segments that have been determined as in Figure 1 above . The analysis result of the Brantas river Ammonia can be seen in Figure 2 below.
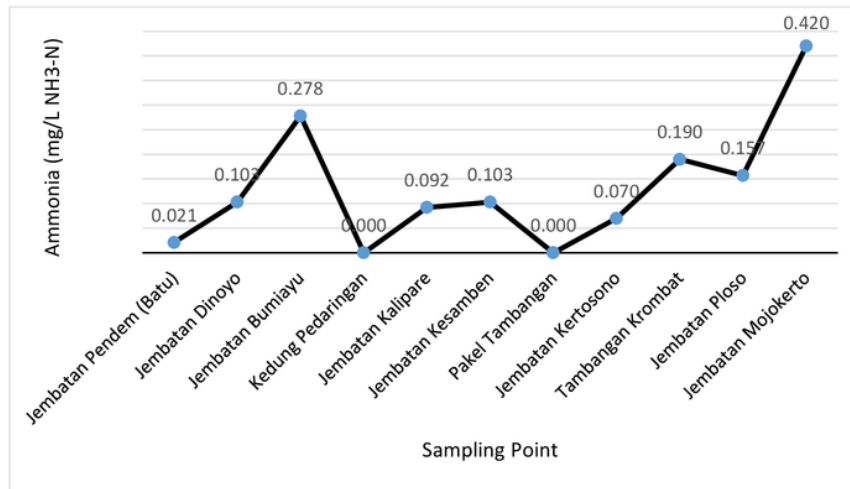
Figure 2 Ammonia Concentration at Brantas River

Ammonia concentration in the Brantas river fluctuates from upstream to downstream as shown in Figure 2 above. The highest Ammonia concentration is found at the Bumiayu Bridge sampling location of 0.278 mg / L. Whereas the Ammonia content at the sampling point location Kedung Pendaringan and Pakel Tambangan Tambangan is not detected. The Brantas River Ammonia concentration comes from domestic, industrial and agricultural pollutants along the river flow. Ammonia is a colorless gas with a sharp odor. Ammonia reacts with water to form a weak base. The term Ammonia refers to two chemical species that balance in water (NH3 instead of NH4 + ions and ions). Ammonia tests usually measure total Ammonia (NH3 and NH4 +). Ammonia Toxicity from NH3. Generally a lot of Ammonia is more toxic at high pH. When dissolved in water, normal Ammonia reacts to form Ammonium ions with the following reactions:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$
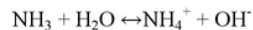
This two-way reaction causes the pH of the water to increase and water to become alkaline. Increasing hydroxyl ions will cause equilibrium to shift to the left and more Ammonia formation occurs. Ammonia and Ammonium quantity depends on pH and temperature. Ammonia is toxic to freshwater organisms at concentrations of 0.53 - 22.8 mg / L. The level of toxicity is directly proportional to pH and temperature. Plants are more tolerant than animals and invertebrates more tolerant than fish. Hatching and growth of fish are affected. Toxic concentrations of ammonia in humans cause loss of balance, convulsions, coma and death (retrieved from http://www.water-research.net/Watershed/ammonia.htm)

Determination value of Deoxygenation Ammonia (K_{NH}) and Ammonia Ultimate (NH_0)

The determination of the value of Ammonia deoxygenation (K_{NH}) and NH_0 by the method of Thomas at each location of monitoring points Brantas river can be seen in Table 1 below and the graph on Figure 3.

The Brantas River Ammonia deoxygenation rates ranges from 0.034 /day to 0,120 / day except at the location of the Kalipare Bridge, the value is unknown because the long-term Ammonia analysis results from day 1 to 30 are zero. The determination value, R^2 is in the range 0.0025 - 0.2227 indicating the suitability of the Thomas method in determining the rates of Ammonia deoxygenation in the Brantas river.

Table 1 Value of K_{NH} and L_0

Location	K_{NH} /day	NH_0 mg/L	R^2
Jembatan Pendem Batu	0,120	0,4581	0,1021
Jembatan Dinoyo	0,114	0,319	0,1575
Jembatan Bumiayu	0,077	3,053	0,044
Jembatan Kedung Pedaringan	0,034	72,508	0,0025
Jembatan Kalipare	-	-	-
Jembatan Kesamben	0,085	1,205	0,1077
Pakel Tambangan	0,091	0,720	0,1378
Jembatan Kertosono	0,095	0,265	0,2227
Tambangan Ngrombot	0,098	37,923	0,0478
Jembatan Ploso	0,095	0,181	0,1288
Jembatan Padangan Mojokerto	0,109	3,146	0,1431
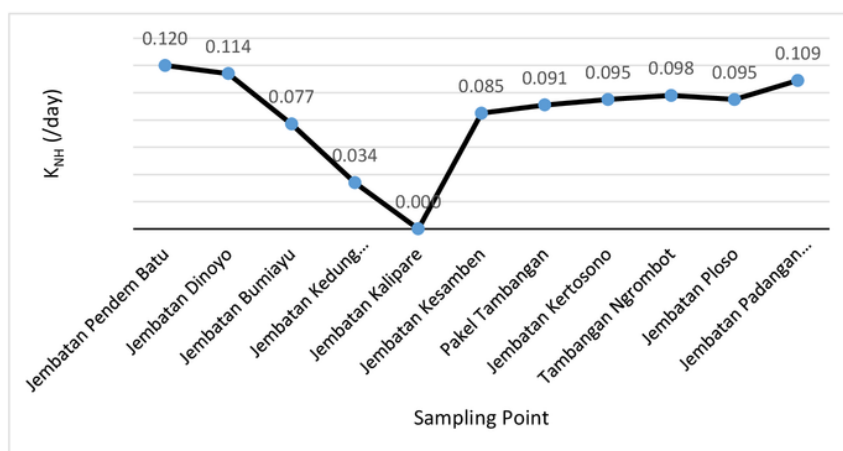
Figure 3 Deoxygenation Rate of Ammonia in Brantas River

The highest value is at the point of monitoring the Jembatan Pendem which is located in the upper reaches of the Brantas River. While the lowest value is at the location of the monitoring point of the Jembatan Kedung Pendaringan. Amonium oxidation is the initial stage and limited rate of the nitrification process. Amonium oxidation can remove 10-80% of antrophogenic polutant substances of Nitrogen. In estuaries, Ammonium oxidation process can reduce the risk of eutrophication when combined with denitrification (retrieved from https://nptel.ac.in/courses/105105048/M9_L12.pdf).

In aerobic environments, Nitrite bacteria (Nitrosomonas) convert Ammonia to Nitrite (NO_2^-) and Nitrate bacteria convert Nitrite to Nitrate (NO_3^-). This process is known as nitrification. The process of Ammonia deoxygenation is carried out by microorganism on the river bed which are rarely carried out by microorganism in the water column. This is due to the slow growth rate. Ammonium oxidizing bacteria tend to attached to particles and settle together. Ammonia archea (AOA) and bacterial (AOB) are oxidizing microorganisms that

have consistent distribution trend in sediments and rarely in the water column. AOA affiliation is a cluster of *Nitrososphaera, Nitrosopumilus and Nitrosotalea*. Generally *Nitrososphaera* is dominant in sediments, while *Nitrosopumilus* and *Nitrosotalea* are dominant in the water column. AOB affiliates include *Nitrosospira, Nitrosomonas*, and *Nitrosospir*a which are dominant in sediments and water columns. Ammonium and Carbon affect the abundance of AOA in sediments (retrieved from uap-bd.edu/ce/nehreen/Lecture%204_CE%20433.pdf). The high level of ammonia deoxygenation rate in the upper Brantas river in Jembatan Pendem, Batu city shows a higher AOA and AOB performance compared to other monitoring point locations. This AOA and AOB performance determines the self-recovery ability of the Brantas river from Ammonia pollutants.

The population of AOA and AOB in wastewater receiving river relates to the level of biological processing. Wastewater without biological treatment contains low abundance of nitrifying organism seeds. The secondary processing will contain high abundance of nitrifying organism seeds so that rate of ammonia oxidation increase (Grouz, 2015). Most of wastewater discharge in Brantas watershade still low performance in biological treatment (Hendriarianti, 2016).

Rate of deoxygenation Ammonia is influenced by Ammonia concentration, temperatur and dissolved oxygen. Temperature Brantas river sample this research measured 25°C and DO are ranged $1,6 - 7,4$ mg /L. Rate of Nitrite oxidation will be greater than Ammonia oxidation in high Ammonia levels at temperatures over 18°C and opposited at low temperatures. Low DO conditions will cause more Nitrite accumulation at high temperatures (Weon, 2004). Temperature of Brantas river is high and DO in some sampling point are low, so it will be more Nitrit in this location. So, the self purification of Brantas from Ammonia need more review from the abundance of AOA and AOB and Nitrit oxidation.

4. CONCLUSIONS

- The Brantas River Ammonia deoxygenation rates ranges from 0.034 /day to 0,120. The determination value, R^2 is in the range 0.0025 - 0.2227.

- The high level of ammonia deoxygenation rate in the upper Brantas river in Jembatan Pendem, Batu city shows a higher AOA and AOB performance.

- The self purification of Brantas from Ammonia need more review from the abundance of AOA and AOB and Nitrit oxidation.

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REFERENCES

[1] I Dewata and Z Adri. 2018." Water Quality Assessment and Determining the Carrying Capacity of Pollution Load Batang Kuranji River". IOP Conf. Ser.: Mater. Sci. Eng. 335 012027

[2] Ming Dou et al.2015. "Measurement and Assesment of Water Resources Carrying Capacity in Henan Provence, China". *Water Science and Engineering*, 8(2): 102e113

[3]   Hua Wang et al. 2015."Fluctuation of the Water Environmental Carrying Capacity in a Huge River-Connected Lake". *Int. J. Environ. Res. Public Health.* 12. 3564-3578; doi:10.3390/ijerph120403564

[4]   Palmer, Mervin D. 2001. *Water Quality Modelling.* Washington DC: The World Bank.

[5]   Haider, H., Ali, W. 2010. "Effect of Wastewater Treatment on Bio-kinetics of Dissolved Oxygen in River Ravi." *Pak. J. Engg. & Appl Sci* 42-51.

[6]   Singh, A.P., et.al. 2007. "Water Quality management of a stretch of river Yamuna: An Interactive Fuzzy Multi-objective Approach." *Water Resource Management, Springer, 21* 515-532.

[7]   Roquibul, Alam, et al. 2006. "Municipal Wastewater Characteristics of Sylhet City Bangladesh." *Electronic Green Journal, 1(23), article 8* 1-12.

[8]   Oke, I.A and Akindahunsi, A.A. 2005. "A Statistical Evaluation of Methods of Determining BOD Rate ." *Journal of Applied Sciences Research 1(2)* 223-227.

[9]   2008. *SNI 6989.57:2008* Metode Pengambilan Contoh Air Permukaan

[10]   Ying Liang, Chunmei Yan, Qing Guo, Jin Xu, Hongzhi Hu.2016." Spectrophotometric determination of ammonia nitrogen in water by flow injection analysis based on NH3- o-phthalaldehyde -Na2SO3 reaction". *Analytical Chemistry Research* 10. 1-8

[11]   Oram, Brian., Ammonia in Groundwater, Runoff, Surface Water, Lakes and Stream, Water research centre, http://www.water-research.net

[12]   https://nptel.ac.in/courses/105105048/M9_L12.pdf

[13]   uap-bd.edu/ce/nehreen/Lecture%204_CE%20433.pdf

[14]   Ludang, Y., Mangkoedihardjo, S. 2009. Leaf area based transpiration factor for phytopumping of high organic matter concentration. Journal of Applied Sciences Research, 5 (10): 1416-1420.

[15]   Mangkoedihardjo, S. 2007. Leaf area for phytopumping of wastewater. Applied Ecology and Environmental Research, 5(1), 37-42.

[16]   Mincong Li, Guangshan Wei,Zheng Gao.2018. "Distict distribution pattern of ammonia-oxidizing archaea and bacteria in sediment and water coloumn of the Yellow River estuary". *Scientific Reports* volume 8, Article number: 1584.

[17]   Najla Aissa-Grouz, Josette Garnier, Gilles Billen, Benjamin Mercier and Anunciacion Martinez.2015. "The response of river nitrification to changes in wastewater treatment (The case of the lower Seine River downstream from Paris". *Annual Limnolology - International Journal Limnology* (51).351–364.

[18]   Hendriarianti E., Karnaningroem N.2016. "Evaluation of Communal Wastewater Treatment Plant Operating Anaerobic Baffled Reactor and Biofilter" *Waste Technology Journal.* Vol 4 (1). 7-12.

[19]   Weon SY, Lee SI, Koopman B.2004." Effect of temperature and dissolved oxygen on biological nitrification at high ammonia concentrations". *Environ. Technol.* Nov;25(11):1211-9. PubMed PMID: 15617436.

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