



Vol. 9 No. 1 (2018) 15-21

**Jurnal Riset
Teknologi Pencegahan Pencemaran Industri**

Journal homepage : ejournal.kemenperin.go.id/jrtppi

**Kementerian
Perindustrian**
REPUBLIK INDONESIA

Removal of ammonia on catfish processing wastewater using horizontal sub-surface flow constructed wetland (HSSFCW)

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ARTICLE INFO

Article history :

Received 15 February 2018

Received in revised form 9 April 2018

Accepted 9 April 2018

Available online 24 May 2018

Keywords :

Horizontal Sub-Surface Flow Constructed
Wetland

Ammonia removal

Catfish processing wastewater

ABSTRACT

The performance of Horizontal Sub-Surface Flow Constructed Wetland (HSSFCW) to remove high ammonia content in catfish processing wastewater was investigated. A rectangular HSSFCW with 6 m long, 3 m wide, 1 m deep and divided into 3 compartments was used. Gravel beds were used as media. *Canna sp.*, *Heliconia sp.*, and *Papyrus sp.* were planted with plant density 10 plants per m². The result showed that removal of ammonia, nitrite and nitrate respectively reached 99.34%, 98.73%, and 99.99%. Residual ammonia concentration can be minimized by improving oxygen transfer rate and lessening organic matter in the system.

1. INTRODUCTION

Small scale industry of catfish processing is one of the emerging small scale industries in Indonesia, increasing in production yield from 39.66% to 67.74% in 2010, with Boyolali, Central Java as one of industrial center area (Triyanti and Shafitri, 2012). Due to its processes, fish processing industries consume large amount of water especially for cleaning and sanitation (Chowdhury et al., 2010), and the wastewater mainly contains variety of organic pollutants, such as lipid, grease, protein, colloidal particles and particulates (Gonzalez, 1996). High ammonia concentration is also observed due to high blood and slime passive content in wastewater streams. The ammonia

concentration normally ranges from 0.7 mg/L to 69.7 mg/L (Fremp, 1994). High ammonia and nitrate discharge in water stream can cause eutrophication (Norton, 2014).

Due to its low cost and relatively easy maintenance, constructed wetland (CW) has been applied as post treatment in many small-scale industrial wastewater treatment plants (Iamchaturapatr et al., 2007). It is typically used after biological treatment for nutrient removal to meet the minimum effluent standard (Moenir et al., 2014) and specifically used as tertiary/post treatment in treating high ammonia content in industrial wastewater (Sun and Austin, 2007). Ammonia removal efficiency in a CW ranges between 25 – 85% (Crites, 1988).

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doi : <https://10.21771/jrtppi.2018.v9.no.1.p15-21>

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Accreditation number : (LIPI) 756/Akred/P2MI-LIPI/08/2016

CW is described as engineered wetlands, contains of saturated or unsaturated substrates, a large biomass of plants, and a large variety of microbial communities, such as nitrifying and denitrifying bacteria (Vymazal, 2014). In theory, many emergent plants could be used for CW. However, in reality, only a limited number of species has been used so far (Vymazal, 2011). In the tropical area, local plants such as *Cyperus papyrus* (Wu et al., 2015; Kyambadde et al., 2004), *Heliconia* and *Canna* (Calheiros et al., 2007; Sohsalam et al., 2008), *Thypha latifolia* (Ciria et al., 2005; Gersberg et al., 1986; Kyambadde et al., 2004) are preferably used. Large variety of microbial communities play major role in the degradation of organic nitrogen, which involve ammonification, nitrification and denitrification mechanisms (Lee et al., 2009). Horizontal Sub-Surface Flow Constructed Wetland (HSSFCW) was selected to achieve higher nitrogen removal. HSSFCW is an engineered constructed wetland with hybrid system, involving a horizontal flow of wastewater feed with the emphasize of waste water level below the surface (Vymazal, 2014).

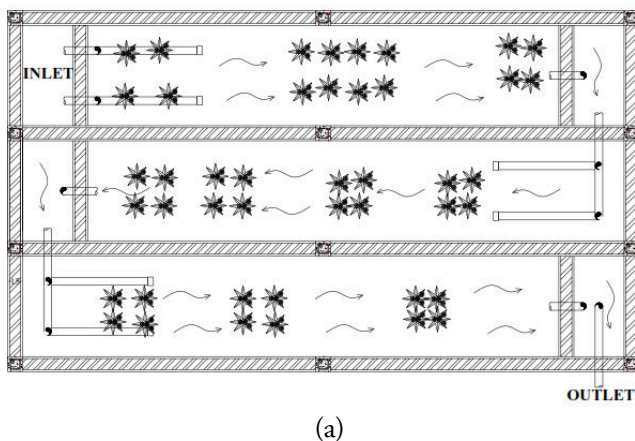
The performance of combination UASB-wetland technology for catfish processing WWTP had already been

studied by Marlana et al. (2017), but this study focused only on the reactor design and the performance of the reactor was only calculated based on COD removal. Due to the fact that ammonia removal efficiency was higher than COD removal, this paper emphasize about nitrogen removal in HSSFCW to treat catfish wastewater.

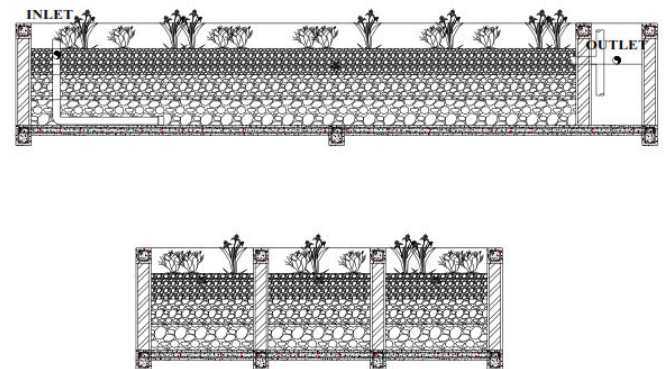
2. MATERIAL AND METHODS

2.1 Material

Wetland used in this study was a rectangular HSSFCW with 6 m long, 3 m wide and 1 m deep. HSSFCW was divided into 3 compartments. Each compartment was filled with gravels to form filter bed. Filter bed was 0.75 m deep, contained of small size gravel ($D = 0.5 - 1$ cm) 0.25 m deep at the top layer, medium size gravel ($D = 1 - 3$ cm) 0.25 m deep at the middle layer and big size gravel ($D = 3 - 7$ cm) 0.25 m deep at the bottom layer. The water level was maintained at 0.7 m deep. The first compartment was planted with *Papyrus sp.*, while the second was planted with *Canna sp.* and the third was planted with *Heliconia sp.* Plant density was arranged 10 plants per m^2 .



(a)



(b)

Figure 1. Constructed Wetland top view(a); side view (b)

2.2 Method

The performance of combination UASB-wetland technology WWTP has been applied in catfish processing industry (Marlana et al. 2017). The wastewater flowed from the outlet of Upflow Anaerobic Sludge Blanket (UASB) reactor into the filter bed via 3-inch polyethylene pipe by gravity. Inlet pipe was embedded at the bottom of filter bed, while the outlet was embedded at the top layer of filter bed. The treated wastewater flowed vertically up, from the bottom to the top layer, then collected in the outlet chamber. The HSSFCW was fed intermittently with flow rate 1 m³/day, during 2 months operational period (May-June 2017). The outlet was then recirculated back (with ratio outlet : recycle = 2:1) to the first compartment using recirculating submersible pump (Aquila P 3900; 43 Watt; H_{max} = 3.9 m; Q_{max} = 2500 L/hour). Recirculating pump was controlled by automatic water level.

Water samples from inlet and outlet of the constructed wetland were collected and periodically submitted to BBTPPI Semarang testing laboratory, and analyzed using the methodology described in Standard Methods (SM) for the Examination of Water and Wastewater (Eaton et al., 2012) for the following parameters: nitrate (NO₃-N, SM-4500-NO₃), ammonia-nitrogen (NH₄⁺-N, SM-4500-NH₃), nitrite (SM-4500-NO₂), alkalinity (SM-2320-alkalinity B), and dissolved oxygen (DO) was measured using SM-4500-O-C. Parameters ammonia, nitrate, nitrite, alkalinity were measured using Thermo Scientific Gallery Automated Photometry instrument, while dissolved oxygen was measured using Brand Digital Burette. Parameters collected on-site including temperature and pH was measured using a pH meter (Krisbow KW06-744).

3. RESULTS AND DISCUSSION

3.1 Removal of ammonia, nitrite and nitrate in the HSSFCW

The removal efficiency of ammonia, nitrite and nitrate in HSSFCW is calculated, meanwhile, the total N concentration is derived from the summation of ammonia,

nitrite, and nitrate concentration. The results of the removal efficiency are shown in table 1.

Table 1. shows that the concentration of all parameters such as ammonia, nitrite, nitrate and total nitrogen (TN) are high, which is dominated by the ammonia concentration. The removal of ammonia, nitrite, nitrate and TN respectively are 66.89 - 99.34%, 26.69 - 98.73%, 35.65 - 99.99% and 59.99 - 99.22%. Those removal efficiencies are higher compared to Vymazal (2001) and Prayitno (2014). Vymazal (2001) reported that ammonia removal efficiency could reach 48.3% and nitrate removal was 38.5%, meanwhile Prayitno (2014) reported 83.67% ammonia reduction. However, the residual ammonia higher concentration than nitrite and nitrate indicated possibility of the nitrification role as limiting step in ammonia removal, which will be discussed further.

3.2 The effect of Alkalinity, Dissolved Oxygen, C/N ratio on nitrification-denitrification process in HSSFCW.

Ammonia (NH₃-N), nitrite (NO₂-N), and nitrate (NO₃-N) removal, alkalinity consumption, and dissolved oxygen (DO) in HSSFCW were monitored and the results are shown in figure 1. Ammonia, nitrite and nitrate removal and alkalinity consumption were calculated from the subtractions of inlet concentration by outlet concentration, while DO was calculated based on DO concentrations in the wetland.

The figure 2. shows that nitrite and nitrate removal are correlated with DO and alkalinity consumption. Nitrite and nitrate removal increase when DO and alkalinity consumption in the system increase, and vice versa. Nitrification is the biological formation of NO₂-N and NO₃-N from NH₄⁺. Oxidation of NH₄⁺ releases H⁺ and drops the pH, while adequate alkalinity is consumed to maintain a neutral pH. Theoretically, 7.14 mg/L alkalinity (as CaCO₃) is consumed for each mg/L ammonia nitrogen, and 1.98 mol of H⁺ is released (Kadlec and Knight, 1996). In this experiment, ratio of alkalinity to NH₄⁺ is ± 4.5:1 mg/L, which is lower than the theoretical stoichiometric calculation written in equation 1.

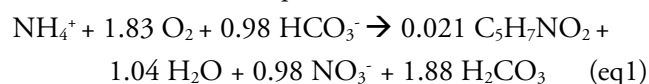
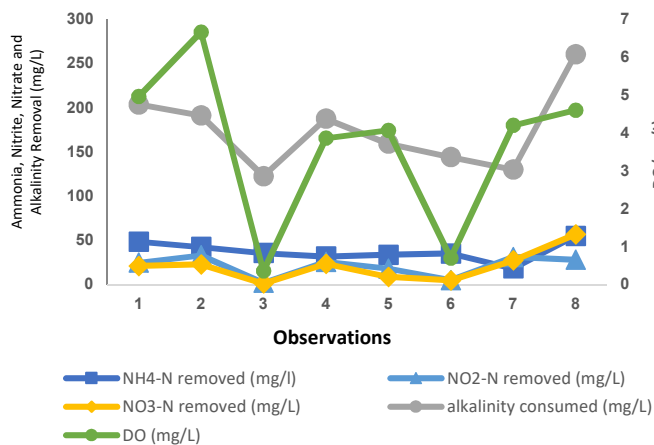
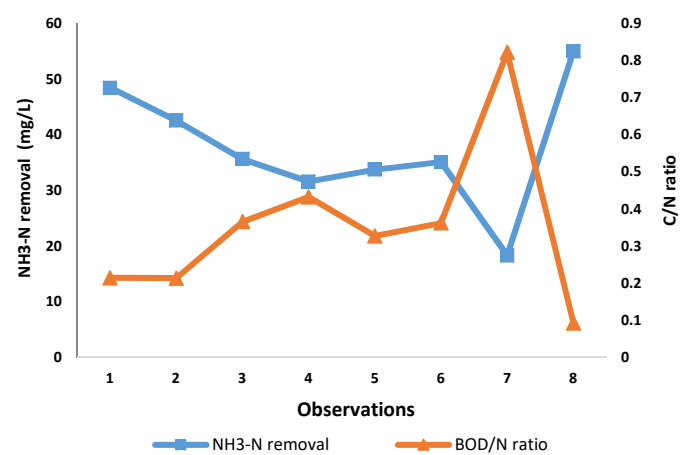


Table 1. Performance of ammonia, nitrite and nitrate in HSSFCW

No.	SAMPLE	Unit	Ammonia	Nitrite	Nitrate	Total Nitrogen(TN)
1	Inlet 1	mg/L	55.4	27.27	30.12	112.79
	Outlet 1	mg/L	7.013	6.26	5.377	18.56
	Removal 1	%	87.34	77.04	82.15	83.46
2	Inlet 2	mg/L	50.2	30.11	33.11	113.42
	Outlet 2	mg/L	7.7	7.42	0.014	15.13
	Removal 2	%	84.66	75.35	99.96	86.66
3	Inlet 3	mg/L	46.8	24.34	26.29	97.43
	Outlet 3	mg/L	15.25	0.82	0.624	16.69
	Removal 3	%	67.41	96.63	97.63	82.87
4	Inlet 4	mg/L	49	23.95	27.81	100.76
	Outlet 4	mg/L	15.3	15.34	9.676	40.32
	Removal 4	%	68.77	35.95	65.21	59.99
5	Inlet 5	mg/L	51.9	4.72	5.75	62.36
	Outlet 5	mg/L	16.3	3.46	3.7	23.46
	Removal 5	%	68.59	26.69	35.65	62.38
6	Inlet 6	mg/L	52.4	12.21	9.464	74.07
	Outlet 6	mg/L	17.35	7.55	4.337	29.24
	Removal 6	%	66.89	38.16	54.17	60.52
7	Inlet 7	mg/L	19.4	32.89	31.2	83.49
	Outlet 7	mg/L	1.12	5.65	0.044	6.814
	Removal 7	%	94.23	82.82	99.86	91.84
8	Inlet 8	mg/L	55.3	57.56	27.97	140.83
	Outlet 8	mg/L	0.365	0.73	0.001	1.096
	Removal 8	%	99.34	98.73	99.99	99.22

**Figure 2.** Ammonia, nitrite, and nitrate removal in correlation with consumption of alkalinity and DO.**Figure 3.** Correlation of Ammonia removal and C/N ratio

A complete NH_4^+ oxidation requires 4.2 – 4.5 mg $\text{O}_2/\text{mg N}$ (Brix, 1987). In HSSFCW oxygen supply is provided by macrophyte, via roots oxygen release. Root oxygen release rates from a number of submerged aquatic plants are reported to be in the range of 0.5 to 5.2 g m^{-2}/day (Sand-Jensen et al., 1982; Kemp and Murray, 1986; Caffrey and Kemp, 1991), specifically according to Bavor et al. (1988), oxygen released by phragmites species was estimated around 0.8 g O_2/m^2 in gravel media. While in this reactor, DO concentrations in the bulk water to support growth of Ammonia Oxidation Bacteria (AOB) could not be calculated precisely due to lack of data. However, the data shows that if residual DO in the effluent is below 1 mg/L (fig. 1), then nitrite and nitrate removal would be decreased. This result agrees with the theory that nitrification reaction occurs in aerobic condition, when DO level drops to <1 mg/L nitrification significantly decrease (Hammer and Knight, 1994). The evidence of low oxygen transfer rate in our system also shown in Figure 3.

Figure 3. shows the correlation of ammonia removal with C/N ratio. C/N ratio was calculated based on the ratio of organic carbon (as BOD) versus ammonia concentration in the inlet. It shows that ammonia removal decreased as ratio C/N in the inlet increased. AOB is autotrophic bacteria which able to consume carbon solely from CO_2 or bicarbonate present in the wastewater under sufficient aerobic condition. However, under oxygen limitation, ammonia removal process is organic carbon limited. Meaning that the presence of high amount of organic carbon (expressed as BOD) limits nitrification process, thus also limits ammonia removal. This is due to the fact that autotroph AOB has much lower respiration rates than heterotroph bacteria (Lee et al., 2009). Hence, significant nitrification performed by AOB does not occur before substantial BOD reduction performed by heterotrophs. It is indication of competition for O_2 between nitrifying bacteria and heterotrophy bacteria which affect nitrification process in the system. The result in this study is similar to the result of (Fan et al., 2013) study, who also performed their study under oxygen limited condition.

4. CONCLUSION

HSSFCW can remove ammonia content in catfish processing wastewater. Removal of ammonia, nitrite, nitrate and TN respectively are 66.89 - 99.34%, 26.69 - 98.73%, 35.65 - 99.99% and 59.99 - 99.22%. Nitrification acts as limiting step in ammonia removal. Hence, to maximize ammonia removal in HSSFCW system, enhancement of nitrification process by increasing oxygen transfer rate and by reducing the amount of organic matter in the system, can give a significant results. Higher oxygen transfer can be achieved by installing an aeration pump or by effluent recycling, while reducing organic matter can be done by optimizing organic removal in the UASB reactor.

ACKNOWLEDGEMENT

This work is financially supported by the grant from DIPA of the Center of Industrial Pollution Prevention Technology (CIPPT) in fiscal year 2016. In addition, our sincere thanks to Mr. Saifuddin who helps us with laboratory analysis and fieldwork.

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