Reaktor

p-ISSN 0852 – 0798
e-ISSN 2407 – 5973

Acredited: SK No.: 60/E/KPT/2016
Website : http://ejournal.undip.ac.id/index.php/reaktor/

Reaktor, Vol. 18 No. 3, September Year 2018, pp. 166-170

Removal of COD and NH_3 from Produced Water using Modified Horizontal Subsurface Flow Constructed Wetlands (HSCW)

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(Received: June 29, 2018; Accepted: August 24, 2018)

Abstract

It is very common that COD and NH_3 are found in Produced Water with elevated concentration. One proven technology that is capable in removing organic substances and nutrients, is Horizontal Subsurface Flow Constructed Wetland (HSCW). Based on characterization of produced water from one oil field in Indonesia, it was shown that COD and NH_3 were found to exceed the threshold limit stated in Ministry of Environmental Decree no. 19 Year 2010. Modified HSCWs were developed in order to treat produced water containing high concentration of COD and NH_3 and allowing anaerobic process to occur in the reactor. The HSCWs were planted by three different species; they were Sagittaria palaefolia (Jasmine Water), Scirpus grossus (Mensiang), and Typha latifolia (Walingi). Organic loading rates (OLRs) to the HSCWs reactor were varied from 7.2 to 72 gr COD/m^2.day. It was found that HSCW planted with Typha latifolia had the highest removal efficiency for both COD and NH_3 when the OLR was set at 14.4 gr COD/m^2.day. Anaerobic bacteria were found in high number indicating that these bacteria involved actively in removing pollutants containing in produced water. However, further microbiology study should be performed in order to determine the role of anaerobic bacteria.

Keywords: *COD; HCSWs; NH_3; organic loading rate; produced water*

How to Cite This Article: Effendi, A.J. and Sandi, R.R., (2018), Removal of COD and NH_3 from Produced Water using Modified Horizontal Subsurface Flow Constructed Wetlands (HSCW), Reaktor, 18(3), 166-170, http://dx.doi.org/10.14710/reaktor.18.3.166-170.

INTRODUCTION

Produced water is formed from the activity of natural gas and crude oil exploration as a result of the separation process (Veil *et al.*, 2004). Produced water contains a number of very high pollutants that are naturally present in underground formations such as organic and inorganic materials, which are toxic, bio-accumulation and bio-concentration and in the long term can be deadly to marine life. Produced water still contains a lot of oil-grease, hydrocarbons (PAHs), heavy metals and anions chloride, phenol, ammonia compounds, and others. Some PAHs such as benzo (a) pyrene, benzo (a) anthracene, 3-methylcholanthrene, 1-nitropyrene is carcinogenic and bacterial mutagens. Phenol compounds are organic compounds that have toxic properties.

Most of the produced water contains high dissolved solids with varying concentration levels.

The most common solid dissolved is salt (sodium chloride). Besides salt, produced water also contains others contaminant such as calcium, magnesium, and potassium with a high enough level, as well as aluminum, antimony, arsenic, barium, boron, chromium, cobalt, iron, magnesium, manganese, nickel, phosphorus, platinum, silicon, strontium, vanadium, uranium, and lead with insignificant concentrations (Reis, 1996). The presence of metals in produced water depends on the wells age and the geological formation where oil and gas are produced. However, there is no significant relationship between the metal concentration contained in crude oil and the concentration of metal contained in produced water (Utvik, 2003).

Table 1. Typical produced water characteristics

Parameter	Unit	Concentration
Density	kg/m^3	1014-1140
Suface Tension	dynes/cm	43-78
TOC	mg/L	0-1500
COD	mg/L	±1220
TSS	mg/L	1.2-1000
TDS	mg/L	100-400.000
pH	-	4.3-10
Total Oil	mg/L	2-565
Volatile (BTEX)	mg/L	0.39-35
Alkalinity	mg/L	<140
Oil and Grease	µg/L	> 275
Chloride	mg/L	80-200.000
Bicarbonate	mg/L	77-3990
Sulfate	mg/L	<2-1650
Ammonium	mg/L	30-300
Sulfite	mg/L	> 10
Total Polar	mg/L	9.7-600
Higher Acid	mg/L	<1-63
Phenols	mg/L	0.009-23
VFA's	mg/L	2-4900

(Source: Guerra *et al.*, 2011)

Produced water treatment using chemical and physical processes are often leaves a layer of oil, color, and odor in the effluent of the plant. Therefore, it is necessary to have wastewater treatment plant that is capable of removing pollutants from wastewater thoroughly. One alternative technology that has a potential to be used in treating produced water is constructed wetlands. Treatment system using constructed wetlands offer an easy and inexpensive alternative compare to traditional wastewater treatment (Mitsch and Gosselink, 2000). Treatment system in constructed wetlands are controlled, designed and built using natural processes that involve vegetation, media, and microorganisms. Provision of pollutants occur in wetland through several kinds of mechanisms such as sedimentation, filtration, volatilization, adsorption, absorption, photolysis, hydrolysis, ionization, oxidation, reduction, and decomposition by microorganisms and uptake by plants (Rodgers and Castle, 2008).

METHODOLOGY

Constructed Wetland Reactor

In this experiment three reactors of horizontal subsurface flow wetland manifold system were used as shown in Figure 1. The horizontal subsurface flow constructed wetlands have high efficiency to eliminate organic pollutants and suspended particles. The reactors consist of 2 processing zones that are separated by a porous septum. Processing zone 1 (Figure 1b) has a depth of 60 cm, whereas processing zone 2 (Figure 1d) has a depth of 80 cm. The function of this difference is to look at the effect of depth on the oxygen concentration in the reactor. Part of the reactor with a depth of 80 cm is expected to have anaerobic conditions allowing the preliminary processes involving anaerobic microorganisms.

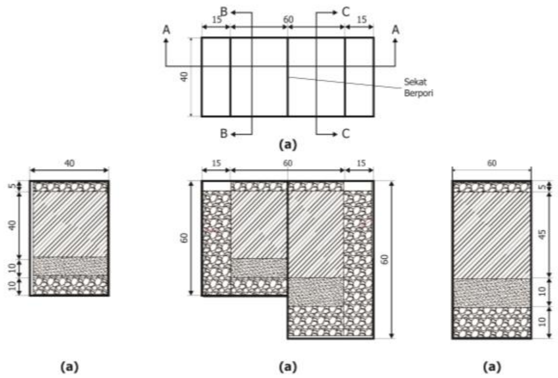

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Figure 1. Lab scale of constructed Wetlands reactor (a) outline, (b) B-B section (Zone 1), (c) A-A section, (d) C-C section (Zone 2)

Constructed Wetland Medium

Planting medium used was a mixture of soil, sand and gravel that were stratified as shown in Table 2. The gravel was placed in the inlet zone to flatten the flow, while at the outlet zone was to avoid mosquito breeding, and placing at the base of the processing zone was to prevent the occurrence of clogging.

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Table 2. Constructed Wetland medium

Media	Size	Type	Depth (cm)	
			Zone 1	Zone 2
Gravel	Ø 20 mm	River Gravel	10	15
Sand	Fine	River Sand	10	15
Soil	Fine	Planting Soil	35	45

Plant

Types of plants used were *Sagittaria palaefolia* (Jasmine Water), *Scirpus grossus* (Mensiang), and *Typha latifolia* (Walingi). These vegetation are water plants, wild and have an economical value. These plants are an annual plant that has a long life so that the plants do not need to be harvested quite often.

Reactor Operation

Produced water was treated in three reactors with 3 variations of plants and 3 organic load variations on the same hydraulic load as listed in Table 3. According to Metcalf and Eddy (1991), the design criteria of hydraulic loading rate for a constructed wetland is 0.045 m^3/m^2.day.

Table 3. Variation of reactor operation

No.	HLR (m^3/m^2.day)	HRT (day)	Flowrate (L/day)	OLR (gr COD/ m^2.day)
1				7.2
2	0.045	7	10.8	14.4
3				72

Samples Sampling & Analysis

Sampling was carried out by Grab method Grab at some sampling points. Sample analyses were carried out in the laboratory. COD and ammonia were monitored daily. In addition, environmental parameters such as pH, DO, and temperature of the sample were also analyzed daily. Methods of analysis are presented in Table 4.

Table 4. Methods and analysis

Parameter	Methods
COD	SNI 06-6989:2-2004 or SNI 06-6989:15-2004 or APHA 5220
Oil & Grease	SNI 06-6989.10-2004
H_2S	SNI 06-2470-1991 or APHA 4500-S^{2-}
Ammonia (as NH_3-N)	SNI 06-6989.30-2005 or APHA 4500-NH3
Total Phenol	SNI 06-6989.21-2005
Temperature	SNI 06-6989.23-2005
pH	SNI 06-6989.11-2004
TDS	SNI 06-6989.27-2005

The number of bacteria present in each media layer was enumerated by using Total Plate Count (TPC) methods. Both aerobic and anaerobic bacteria were calculated only suspended growth bacteria.

RESULTS AND DISCUSSION

Produced Water Characteristics

Produced water was used in this study came from one area of gas exploration and production in Indonesia. This water comes from the separation between the gas phase, oil, and water from drilling in the exploration and production area. The produced water characteristics were shown in Table 5.

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Table 5. Produced water characteristics

Parameter	Unit	Concentration	Standard*)
COD	mg/L	1528	200
BOD	mg/L	545	-
pH	-	6.87	6-9
NH_3	mg/L	19.6	5
Oil & Grease	mg/L	17.5	25
TDS	mg/L	445	4000
Conductivity	µS/cm	612	-
Phenol	mg/L	0.095	2
H_2S	mg/L	0.171	0.5
TSS	mg/L	75	-

*)Ministry of Environmental Regulation no. 19/2010

As shown in Table 4, parameters that have exceeded the quality standard was COD and ammonia. According to Guerra *et al*. (2011), the average COD concentrations in produced water is usually around 1220 mg/L, whereas as for ammonia generally the concentration is in the range of 30 mg/L to 300 mg/L.

COD Removal

According to Vymazal and Kropfelova (2009), the optimum organic loading rate (OLR) on the horizontal subsurface constructed wetlands is in the range of 5-20 g COD/m^2.day. In this study, the OLR were varied between 7.2 and 14.4 g COD/m^2.day and 72 g COD/m^2.day to adjust the initial COD concentration of the waste produced water was approximately equal to ± 1600 mg/L. According to Veil *et al.* (2004), the presence of organic matter in produced water is dominated by a combination of typical aromatic compounds found in petroleum formation. Figure 2 shows the amount of COD removal efficiency in the variation of OLR and type of crops.

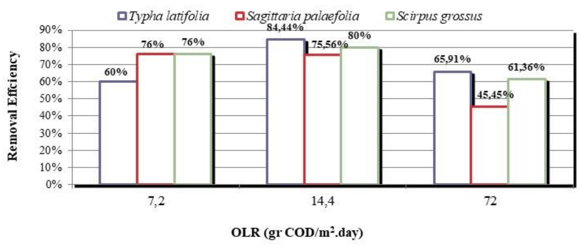

Figure 2. COD removal under various OLR

It can be seen in Figure 2 that the optimum COD removal efficiency was found around 84% in OLR of 14.4 g COD/m^2.day that was planted with *Typha latifolia*. In general, the COD removal efficiency in constructed wetlands increased with the increase of organic loading as demonstrated in the CW reactor planted with *Typha latifolia* and *Scirpus grossus*. However, optimum efficiency was achieved when OLR between 14.4-72 g COD/m^2.day. Different CW behavior was found in the reactor planted with *Sagittaria palaefolia*. COD removal efficiency decreased with the increase of OLR. It was likely *Sagittaria palaefolia* would only allow a lower OLR for its growth. Organic compound removal efficiency in CW was also affected by the ratio of BOD/COD. When the ratio of BOD/COD was higher than 0.5, the produced water could be classified as biodegradable waste. The ratio of BOD/COD in produced water used at steady conditions is shown in Table 6.

Table 6. BOD/COD ratio under steady state condition

OLR (gr COD/m^2.day)	COD In (mg/L)	BOD In (mg/L)	BOD/COD Ratio
72	1365	530	0.39
14.4	270.72	145.5	0.54
7.2	160	66	0.41

When OLR was 14.4 gr COD/m^2.day, the ratio of BOD/COD was greater compared to the two other load variations. This indicates that under OLR of around 14.4 gr COD/m^2.day, the treated produced water was more biodegradable than the other load variations.

Ammonia Removal

Ammonia is the most common form and the most important classes of compounds of nitrogen contained in the wastewater. Ammonia is toxic to aquatic animals, so that ammonia including harmful to the environment. Ammonia is a compound commonly found in formations taken from wells producing oil and gas. Ammonia can be easily soluble in water, and easily evaporates into the air if the pH of the water increases. When ammonia water soluble chemical reaction in which ammonia acts as a base from which to obtain hydrogen ions from H_2O to produce ammonium ion ($NH4^+$) and hydroxide ions (OH^-).

According to Vymazal (2007), the optimum condition for nitrogen load in HSCWs is 1.2 gr NH_4-N/m^2.day. The absorption of nitrogen by plants in the wetland is only about 10-16%, of nitrogen compounds dissolved in water (Gertsberg *et al.*, 1983). Most of the removal of nitrogen compounds carried out by the bacteria through a process of ammonification, nitrification, and de-nitrification. OLR variation also leads to change in ammonia load. In this study, the measured ammonia load for each variation was from 0.93 to 1.05 gr NH_4-N/m^2.day (OLR of 7.2 gr COD/m^2.day), 0.68 to 0.79 gr NH_4-N/m^2.day (OLR 72 gr COD/m^2.day), and 0.19 to 0.22 gr NH_4-N/m^2.day (OLR of 14.4 gr COD/m^2.day). The ammonia removal efficiency under various OLR can be seen in Figure 3.

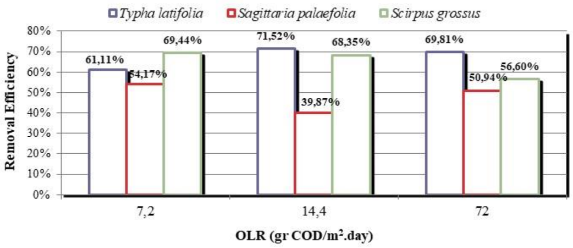

Figure 3. Ammonia removal under various OLR

It can be seen that on average ammonia removal efficiency was found better in the condition of OLR of 7.2 gr COD/m^2.day or under ammonia loading at around 0.93-1.05 gr NH_4-N/m^2.day. CW with *Typha latifolia* showed a negative response to the increased load, wherein the resulting efficiency decreased with increasing ammonia load. While CW planted with *Sagittaria palaefolia* demonstrated a positive response to the increasing load. However, the overall removal of CW with *Typha latifolia* was far better compared to CW with *Sagittaria palaefolia*. According to Clarke and Baldwin (2002), *T. latifolia* is a plant that is quite tolerant of high ammonia load. The removal of ammonia in CW was also affected by C/N ratio existing in the reactor. Table 7 indicated the C/N ratio at the reactor under steady-state conditions.

Table 7. C/N ratio under various OLR

OLR (gr COD/m^2.day)	COD In (mg/L)	NTK In (mg/L)	C/N Ratio
7.2	160	21.92	5.47
14.4	270.72	7.96	45.35
72	1365	26.53	38.59

The differences C/N ratio was quite significant among the three OLR variations. The optimum condition of C/N ratio in CW is around 5 and consistent as showed with the result of this study. CW reactors which were planted with *Scirpus grossus* and *Sagittaria palaefolia* achieved maximum ammonia removal efficiency when C/N ratio of about 5.47 or at OLR of 7.2 gr COD/m^2.day. However, CW with *Typha latifolia* demonstrated the smallest efficiency when the C/N ratio was 5. This suggested that the *Typha latifolia* was required large C/N ratio compared to others plant.

Table 8 shows the final effluent quality under the most optimum condition (OLR of 14.4 gr COD/m^2.day). It can be seen that the reduction of ammonia resulting in the increase of Nitrite and Nitrate. Overall, it could be concluded that under OLR 14.4 gr COD/m^2.day with *Thypa Latifolia*, the treated water has best quality and met the effluent standard regulated by Ministry of Environment Decree no. 19/2010.

Table 8. Final effluent quality under optimum condition

Parameter	Unit	Influent	Effluent *Typha L*
pH	-	7.13	6.85
Conductivity	µS/cm	333.00	354.00
TDS	mg/L	270.00	193.00
Ammonia	mg/L	4.56	1.30
Nitrate	mg/L	0.02	0.04
Nitrite	mg/L	0.01	0.02
NTK	mg/L	7.96	1.59
N-Organic	mg/L	3.33	0.23
Phenol	mg/L	0.04	0.02
Sulphide	mg/L	0.06	0.02
COD	mg/L	270.72	42.11
BOD	mg/L	145.00	10.32
TSS	mg/L	5.00	1.00
Oil & Grease	mg/L	3.40	0.80

The Presence of Microorganisms

Pollutants removal in a Constructed wetland involves the role of the various populations of microorganisms including bacteria, fungi, and algae. These microorganisms have an important role in the transformation of pollutants that helps constructed wetlands in treating produced water. The number of aerobic microorganisms, especially in soil media both in zone 1 and zone 2 in each variation was much more than that found in the sand and gravel medium (Figure 4). In addition, the number of aerobic microorganisms in the soil of zone 1 which ranged between 15000-29400 CFU/mL, was higher when compared with the number of microorganisms in the same media of zone 2 which only ranged between 5700-19700 CFU/mL.

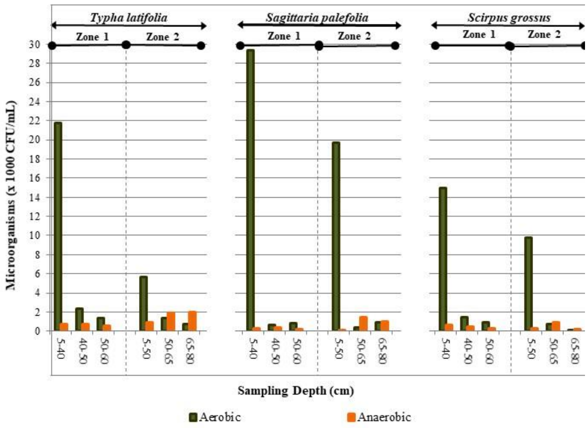

Figure 4. The presence of microorganisms

The microorganisms involved in the constructed wetlands processes are mostly located in the root zone of plants, especially for aerobic microorganisms that are mostly attached to the roots of plants wherein oxygen demand is fulfilled. This resulted in the number of microorganisms that exist in the soil media was much more abundant than the number of microorganisms present in others media. The presence of microorganisms in CW with *S. palaefolia* was more abundant when compared to the number of microorganisms in *T. latifolia* and *S. grossus* especially for aerobic microorganisms. The deepest the location was, the more the presence of anaerobic microorganisms. The shortage of free oxygen as electron acceptor causing the anaerobic microorganisms was more dominant. This result also showed that in a wetland system, anaerobic microorganisms group were also participated actively in the process. Since this CW was designed as horizontal subsurface flow type, the aeration process was occured. It is clear that the abundance of aerobic microorganism due to good aeration system making O_2 as electron acceptor always available during the process.

CONCLUSIONS

Based on the study results of produced water treatment from one field of Oil and Gas industry in Indonesia by using the Horizontal Subsurface Constructed Wetland, it could be seen that the use of this technique was proven in reducing COD and ammonia to achieve quality standards stated in Environmental Ministry decree no: 19/2010. The optimum conditions were achieved in Organic Loading Rate (OLR) of 14.4 gr COD/m^2.day by using *Typha latifolia* plants. The COD and Ammonia removal efficiency achieved were 85% and 72% respectively. HSCW related studies conducted by various sources of wastewater as well as the variation of OLH and HLR shows that the efficiency of COD and Ammonia were in the range of 40-95% and 20-85% respectively. The presence of both aerobic rhizobium bacteria and also anaerobic microorganisms indicated the involvement of these microorganisms during the removal of COD and Ammonia.

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