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Effluent treatment of pharmaceutical industry by using subsurface flow wetland system

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Abstrack - *Constructed wetland is one of the alternatives to increase water quality before it flowed into waterways. Sub Surface Flow Wetland System is one type of the constructed wetland for waste water treatment which is using symbiotic relation between water plants and microorganism around rooting system (rhizosphere) in media.* Cyperus alternifolius *and* Canna indica, L. *as well as gravel and sand media are plants and medias that can be used in constructed wetland. This research aimed to analyze the effectiveness of plant species between* Cyperus alternifolius *and* Canna indica, L. *as well as the effectiveness of gravel and sand media to decrease nitrite, ammonia, BOD, and COD concentrations. Four reactors SSF-Wetlands with dimension of 120 cm x 30 cm x 50 cm were used in this research. The study was conducted over 12 days following the acclimatization of plants for 7 days. Data analysis were performed by comparing the degradation coefficient (k) of BOD, COD, nitrite, and ammonia concentrations with retention time of the effluent. The results showed that the degradation coefficient for the reactor with gravel media and Cyperus* alternifolius *for nitrite variable was 0.60, ammonia 0.49, BOD 0.45, and COD 0.36.* Cyperus alternifolius *have a higher effectiveness in reducing the concentration of nitrite, ammonia , BOD and COD than* Canna indica , L. *Reactors with gravel media have higher effectiveness in reducing BOD , COD , ammonia and nitrite concentration than sand media.*

Keywords : Canna indica. L. , Cyperus alternifolius, *SSF - Wetland, , WWTP effluent of pharmaceutical industry*

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Introduction

The effort to manage the environment has been implementing by all parties, industries included, as a way to promote sustainable development. The sustainable development is a mindful and planned effort which mixed environment aspect, social, and economy into development strategy to ensure the integrity of environment for this generation and the next (UU no 32, 2009). Waste Water Treatment Plan (WWTP) is a way to increace wastewater quality before it flowed into water ways. Khiatuddin (2003), there were so many advantages that we could get from waste water treatment. The treatment waste water will be able be used to water the plants and fishery. It is useful to add water reserved. To minimize and utilize the effluent from WWTP of pharmaceutical industry, constructed wetland system can be an alternative to increace the effleunt quality.

There are two types of constructed wetland, they are Surface Flow and Sub Surface Flow. Sub Surface Flow System is one of the constructed wetland for waste water treatment which used symbiotic relation between water plants and microorganism around rooting system (Rhizosphere) in media. Organic material in waste water will be reformed by the microorganism to become simpler compound and it will be used by plant as their nutrient, whereas water plant rooting system will produce oxygen which will be used as energy/catalyst in metabolism process for microorganism's life (Supradata, 2005).

SSF-wetland is one of alternative to treat waste water with low operational and maintenance cost (Saeed, Tanveer and Sun, Guangshi, 2012). There are many components in constructed wetlands include water, substrate, plants, and microorganism. The processes that affect removal and retention of nitrogen during wastewater treatment in constructed wetlands are manifold and incluce NH3 volatilization, nitrification, denitrification, nitrogen fixation, plant and microbial uptake, mineralization (ammonification), nitrate reduction to ammonium (nitrate-ammonification), anaerobic ammonia oxidation (ANAMMOX), fragmentation, sorption, desorption, burial, and leaching (Vymazal, 2007).

The plant that can be used as wetland such as Cyperus alternifolius and Canna indica, L.. Those plant can be used as ornamental plants for waste water treatment by constructed wetland. According to the research that Supradata done in 2005 for treating domestic waste water, Cyperus alternifolius is able to decreas BOD and COD concentration.

This research aims to analyse which media and plant that more effective in WWTP effluent treatment from pharmaceutical industry for BOD, COD, ammonia, and nitrite of water quality. Generally, the result hopefully can be used as study material for continual waste water treatment system by using constructed wetland system, primarily SSF-wetland, and also can be made as an alternative of WWTP effluent treatment from pharmacy industry in order to minimize waste water disposal to waterways, as a way to improve water quality as clean water from WWTP effluent.

Experimental Methods

The research stage is divided into three steps, they are preparation, execution, and data analysis. 4 reactors of SSF-Wetlands were prepared with dimension 120 cm x 30 cm x 50 cm were used in this research. The reactors was made of wood structure which covered with plastic. Two evaporated reactors contained gravel and sand in each reactor,with 60 cm x 30 cm x 50 cm, pipe, hose, valve, 600ml plastic bottle. The 3 months age of Cyperus alternifolius and Canna indica,L., the effluent of WWTP pharmaceutical industry, gravel and sand were used as material. The average diameter of the sands was 1-5 mm (Supradata, 2005) and gravel 10-25 mm (Kamarudzaman, Hafiz, Aziz, Jalil, 2011).

The next step is plant acclimatization. The plant acclimatization was done in seven days by filling water tap to reactor. Water sample taking from reactor outlet was done in every two or three days. The water sample was filled into plastic bottle and then was analysed the BOD, COD, nitrite and ammonia. The volume of the WWTP effluent was flowed into the gravel reactor was 48 litres/reactor and for sand media was 20 litres. This differences was according to porosity differences between sand and gravel.

The independent variable consisted of the type of the plant that be used, Cyperus alternifolius and Canna indica, L and also sand and gravel as media. The dependent variables were the concentration of COD, BOD, nitrite and ammonia from SSF wetlands reactor batch system. This research was done in laboratory scale with water quality analysis was done in laboratory Environmental Engineering Major of Diponegoro University.

Data analysis was performed using microsoft excel to create a graph of the relationship of each variable concentrations (nitrite, ammonia, BOD and COD) of the wastewater residence time in the reactor with an exponential equation.

$$y = C_0 e^{-kt}$$

The analysis was done by comparing the degradation constanta (k) in the exponential equation between reactors with *Canna indica, L.* and *Cyperus alternifolius* as well as sand and gravel media. Purwanto (2004), degradation constanta (k) illustrates the magnitude of the degradation rate of organic matter.

Results and Discussion

Nitrite Concentration

Figure 1 shows nitrite concentration degradation in reactor with *Canna indica, L.* and *Cyperus alternifolius* as well as gravel and sand media. Line equation that shows the function of nitrite degradation in each reactor as presented on Table 1.

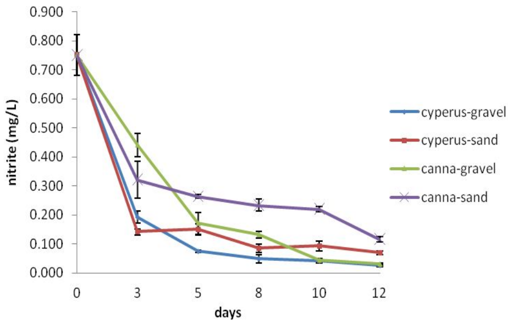

Figure 1. Nitrite Concentration at Various Reactors

Table 1

Exponential Equations of Nitrite Degradation

No	Reactor	Exponential Equation	Degradation Constanta
	Gravel Media		
1.	*Cyperus alternifolius*	$y = 0.751e^{-0.60x}$ $R^2 = 0.893$	0.60
2.	*Canna indica, L.*	$y = 0.751e^{-0.50x}$ $R^2 = 0.911$	0.50
	Sand Media		
3.	*Cyperus alternifolius*	$y = 0.751e^{-0.45x}$ $R^2 = 0.698$	0.45
4.	*Canna indica, L.*	$y = 0.751e^{-0.29x}$ $R^2 = 0.865$	0.29

Table 1 shows exponential equation of nitrite degradation rate of reactor with *Cyperus alternifolius* is higher *than Canna indica, L.* both in reactor with gravel and sand media. Degradation constanta (k) for reactor with gravel and sand media shows that *Cyperus alternifolius* has a higer result than *Canna indica, L.* In reactor with gravel media, degradation constanta of reactor with *Cyperus alternifolius* is 0.6 and *Canna indica, L.* is 0.5. Meanwhile, in the reactor with sand media, degradation constanta of reactor with *Cyperus alternifolius* is 0.45 and *Canna indica, L.* is 0.29.

These results show that the degradation rate of nitrite concentration in reactor with *Cyperus alternifolius* is faster than *Canna indica, L.* Degradation constanta (k) in exponential equation shows the degradation rate of organic matter (Purwanto, 2004).

According to Khiatuddin (2003), plants can absorb ammonium and nitrate ions in solution, but nitrite can not be absorbed by root, even dangerous. According to Cui, Ouyang, Yang, Chen, Zhou, and Lou (2010), nitrogen degradation in the constructed wetland is due to the contact and interaction between nutrients, substrates, and plant roots.

Plants can't absorb nitrite. Therefore, nitrification and denitrification processes play a role in nitrite degradation in SSF wetland reactor. Nitrification is the biological oxidation of ammonium to nitrate with nitrite as a intermediates reaction (Vymazal, 2007). There are two processes in nitrification. The first reaction is oxidation of ammonium to nitrite by Nitrosomonas chemolithotropic, Nitrosocossus, and Nitrosospira bacteria. The second stage is the oxidation of nitrite to nitrate by Nitrobacter and Nitrospira bacteria (Saeed and Sun, 2012). Optimum pH for nitrification process is 6.6-8 (Cooper, et al, 1996 in Vymzal, 2007). Denitrification process is nitrate converted to nitrogen gas (N_2), nitrous oxide (N_2O), and nitric oxide (NO) with facultative bacteria Bacillus, Pseudomonas, Enterobacter, Micrococcus, and Spirillim (Kadlec and Knight, 1996 in Saeed and Sun, 2012).

From the nitrification process, nitrate is formed from nitrite oxidation by Nitrobacater bacteria so that the plants can absorb nitrate. Nitrite concentration can decrease. *Cyperus alternifolius* has a higher efficiency than *Canna indica, L.*, because the surface area of *Cyperus alternifolius* roots to absorb nitrogen is greater than *Canna indica, L.* .

Organic matter degradation in the wetland reactors is affected by microorgnism activity and decomposition of organic matter by plants. Abiotic processes (physical and chemical) or biotic (microbial and plant) and a combination of both processes play a role in the artificial wetland system (USDA and ITRC in Supradata, 2005). According to Wood in Tangahu and Warmadewanthi (2001), decreasing concentration of organic matter in the wetland system is due to the mechanism of the microorganisms activity and plants, through the process of oxidation by aerobic bacteria that grow around the plant rhizosphere and the presence of heterotrophic bacteria in the wastewater. According Khiatuddin (2003), nitrogen is a important element in the formation of amino acids which in turn form a complex protein compounds that are important on body structure of living things, including plants. Plants can only absorb ammonium and nitrate ions in solution, but nitrite can not be absorbed by plant roots, even dangerous. Therefore, the nitrite degradation process is influenced by nitrification process in the reactor.

Figure 1 shows that nitrite concentration degradation by gravel media has a higher efficiency than sand media. This is due to the porosity of the media will affect the performance of SSF-wetland (Wibisono and Masrevaniah, 2008). Porosity will affect the oxygen supply into the reactor. In the process of organic materials decomposition in the SSF wetland reactor, aerobic bacteria play a role in outlining the existing organic matter. Therefore, the presence of oxygen in the reactor must be considered.

Ammonia Concentration

Figure 2 shows the ammonia concentration degradation in various types of reactor. Function of ammonia degradation in each reactor as presented on Table 2.

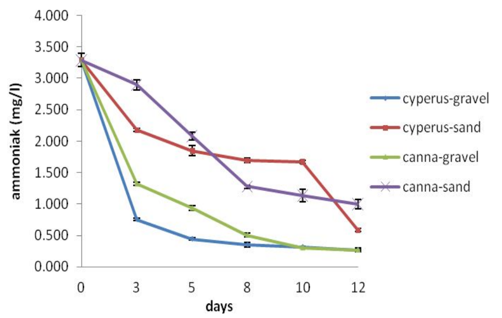

Figure 2. Ammonia Concentration at Various Reactors

Tabel 2. Exponential Equations of Ammonia Degradation

No	Reactor	Exponential Equation	Degradation Constanta
	Gravel Media		
1.	*Cyperus alternifolius*	$y= 3.292e^{-0.49x}$ R^2=0.762	0.49
2.	*Canna indica, L.*	$y= 3.292e^{-0.44x}$ R^2=0.943	0.44
	Sand Media		
3.	*Cyperus alternifolius*	$y= 3.292e^{-0.20x}$ R^2=0.736	0.20
4.	*Canna indica, L.*	$y= 3.292e^{-0.19x}$ R^2=0.876	0.19

The above equation shows the same result that reactor with gravel media has a higher degradation canstanta (k) than sand media both in reactor with *Cyperus alternifolius* and *Canna indica, L.* Both reactor with sand and gravel media shows that degradation rate of *Cyperus alternifolius* is higher than *Canna indica, L.* In reactor with gravel media, constanta degradation (k) of reactor with *Cyperus alternifolius* is 0.49 and *Canna indica , L.* is 0.44. In the reactor with sand media, degradation constanta of reactor with *Cyperus alternifolius* is 0.20 and *Canna indica , L.* is 0.19. These results indicate the degradation rate of ammonia with *Cyperus alternifolius* is faster than the reactor with *Canna indica , L.*

Ammonia degradation in SSF wetland reactor is affected by absorption by plant roots and nitrification process. In the nitrification process, ammonia is oxidized to nitrate. Ammonia and nitrate can be absorbed by plants (Khiatuddin, 2003). Both reactor with sand and gravel media shows *that Cyperus alternifolius* have higher degradation rate than *Canna indica, L.* Surface root area of *Cyperus alternifolius* is greater than *Canna indica, L.* that will affect the availability of oxygen for ammonia and nitrate uptake area by plant roots.

Nitrogen degradation in wetland system occurs due to the absorption of nitrogen compounds by plants directly (Gersberg, 1985 in Abdulghani, 2013). Ammonia degradation can occur due to direct absorption by the plant as well as the processes of nitrification and denitrification by microorganisms. Gravel media has a higher effectiveness than sand media. This is due to the absorption of ammonia directly by the plant as well as the nitrification process that oxidizes ammonium to nitrate. Nitrate can also be absorbed by plants.

COD Concentration

Figure 3 shows that reactor with *Cyperus alternifolius* has a higher ability on COD degradation than *Canna indica,L.* both on gravel and sand media. Gravel media has a higher ability to reduce COD concentration than sand media. Here is the equation that shows the degradation of COD in wastewater residence time in each reactor.

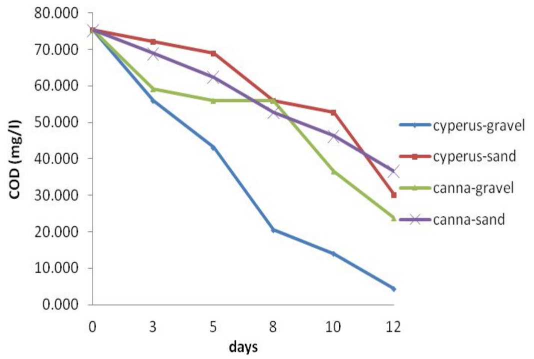

Figure 3. COD Concentration at Various Reactors

Tabel 4.3

Exponential Equations of COD Degradation

No	Reactor	Exponential Equation	Degradation Constanta
	Gravel Media		
1.	*Cyperus alternifolius*	$y= 75.25e^{-0.36x}$ R^2=0.804	0.36
2.	*Canna indica, L.*	$y= 75.25e^{-0.14x}$ R^2=0.763	0.14
	Sand Media		
3.	*Cyperus alternifolius*	$y= 75.25e^{-0.09x}$ R^2=0.640	0.09
4.	*Canna indica, L.*	$y= 75.25e^{-0.09x}$ R^2=0.858	0.09

The results above show the degradation rate of *Cyperus alternifolius* 0.36 (gravel media) and 0.09 (sand media) is higher than *Canna indica, L*. These results indicate that the rate of COD degradation in the reactor with *Cyperus alternifolius* is faster than *Canna indica, L.*
The above equation also shows the same result, gravel media has higher degradation coefficient than sand media 0.36 (Cyperus) and 0.14 (Canna). The effectiveness is indicated by the efficiency of COD concentration removal based on the type of plant. Gravel media has better efficiency than the reactor with sand media. The process of organic matter degradation in SSF-wetland influenced by mechanisms within wetland and activity of microorganisms. The degradation is influenced by the availability of oxygen for biological processes. The availability of oxygen in the root make the number of microorganisms which act to degrade the wastewater greater (Nurul and Aditya, 2010).

BOD Concentration

Figure 4 shows that reactor with *Cyperus alternifolius* and gravel media has a higher effectiveness in reducing BOD concentration than *Canna indica , L.* and sand media. Here are the equation that shows the relationship between BOD concentration in the reactor and residence time of wastewater.

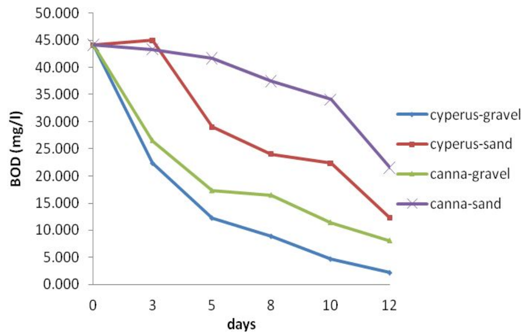

Figure 4. BOD Concentration at Various Reactors

Tabel 4.4

Exponential Equations of BOD Degradation

No	Reactor	Exponential Equation	Degradation Constanta
	Gravel Media		
1.	*Cyperus alternifolius*	$y= 44.16e^{-0.45x}$ R^2=0.932	0.45
2.	*Canna indica, L.*	$y= 44.16e^{-0.27x}$ R^2=0.942	0.27
	Sand Media		
3.	*Cyperus alternifolius*	$y= 44.16e^{-0.16x}$ R^2=0.778	0.16
4.	*Canna indica, L.*	$y= 44.16e^{-0.07x}$ R^2=0.581	0.07

From the above equations were compared degradation coefficient (k) by classifying reactor based on the media. Both reactors with sand and gravel media shows that *Cyperus alternifolius* has a higher degradation coefficient than *Canna indica , L.* is equal to 0.45 (gravel media) and 0.16 (sand media). Regression coefficient (R^2) for the Cyperus reactor is 0.932 (gravel media) and 0.778 (sand media). It shows there is a correlation between BOD reduction and wastewater residence time in the reactor. Exponential equation of BOD degradation shows BOD degradation rate of reactor with gravel media is faster than sand media both in reactor with *Cyperus alternifolius* and *Canna indica, L.*

pH

PH measurement is done while taking water samples from the reactor SSF-Wetland.

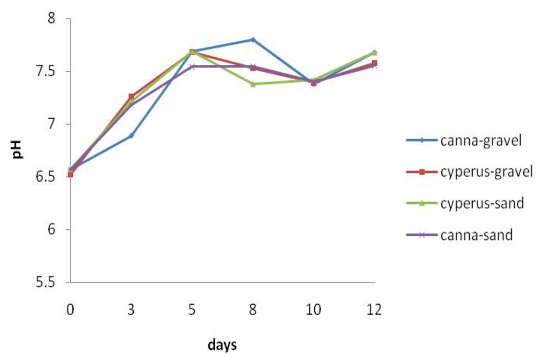

Figure 5. pH

Overall, pH of the water in each reactor fulfill water quality standards according to the PP. 82, 2001, ie at pH 6-9. pH for all reactors ranged from 6.57 to 7.69. With the neutral pH value of wastewater, process of photosynthesis can run well (Abdulghani , 2013). Photosynthesis process by plants often create high pH value during the day. The pH of shallow flood water is greatly affected by the total respiration activity of all the heterotropis organisms and photosynthesis of the species present (Vymazal, 2007). The formation of ammonium ions (NH_4^+) of ammonia (NH_3) can increase the pH value (Campbell and Reece, 2010). According to Faulwetter, Gagnon, Sunber, Chazarenc, Burr, Brisson, Camper, and Stein (2009), Environmental factors affecting microbial growth and N and S cycles are temperature, pH, salinity, the species, and the availability of organic carbon.

According to Kadlec and Knight in Zhang, regal, and meney (2009), every wetland plants can have different capacities in the assimilation of nutrients in the wastewater. Differences of nutrients accumulation between species indicated by the difference in the stages and the efficiency of absorption as well as utilization of nutrients. Zhang, regal, and meney (2009), nutrient absorption capacity related to habitat and influenced by roots and rizhom. Habitat differences also relate to other factors, there are temperature, aeration, pH, sulfide , and nutrient composition in solution, plant growth stage, form symbiotic capacity with bacteria or fungi.

Canna indica, L. and *Cyperus alternifolius* are monocotyl plants. The difference absorption capability of nitrite, ammonia, BOD, and COD is due to the differences in the ability of the roots. Plant roots also play a role in the oxygen supply in the reactor that used by microorganisms to degrade the wastewater.

To ensure the life of microorganisms can grow well, then oxygen transfer from the roots of the plant must be able to meet the need for the life of microorganisms. The availability of oxygen in the media will be supplied by the plant roots, which is a byproduct of photosynthesis process of plants. Aerobic conditions in the root system area (rhizosphere) and aerobic microorganisms are depend on the oxygen supply of the root system of plants in the SSF–Wetlands (Supradata, 2005)

Porosity of the media affects the performance of wetland plants. According to research conducted by Wibisono and Masrevaniah in 2008 which showed that the artificial wetland system with a water garden plants (TTA) with mixed of gravel media and plastic glasses that have a higher porosity, produces better performance compared to TTA with gravel media which have lower porosity. Gravel media has a greater porosity than sand media. The porosity of the media will affect to the availability of oxygen in the reactor. Thus, the availability of oxygen in the reactor through a medium porosity will affect the performance of SSF wetland.

Conclusion

Cyperus alternifolius have a higher effectiveness in reducing the concentration of nitrite, ammonia, BOD, and COD than *Canna indica, L*. Reactors with gravel media have higher effectiveness in reducing BOD, COD, ammonia, and nitrite concentration than sand media .

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