The Effectiveness of Heavy Metals Pb, Cd and Zn Reduction in NPK Fertilizer Waste Combined with Biofilters of Seaweed (Gracillaria sp.), Blood Clam (Anadara sp.), and Zeolite

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Abstract. The heavy metals Cadmium Cd, Pb and Zn in fertilizer factory waste in aquatic environment enables toxic level of metal concentration for the life of aquatic organism. The metal-polluted aquatic environment potentially affect is surroundings. This study aims to find out the effectiveness of the reduction of the heavy metals Cd, Pb and Zn by using a biofilter combination of seaweed (Gracillaria sp.), blood clam (Anadara sp.) and zeolite. This study used biofilter combination between seaweed (Gracillaria sp.), and blood clam (Anadara sp.) with different concentration for each treatment. The result of this study shows that the proper use of biofilter combination can reduce the content of heavy metals Cd, Pb and Zn in NPK fertilizer factory waste. The initial contents of heavy metals Cd, Pb and Zn in NPK fertilizer factory waste were 0.01058 mg/L, 1.155 mg/L and 1.38 mg/L respectively, which were reduced into 0.0205 mg/L, 0.0736 mg/L and 0.0283 mg/L. Heavy metals Cd and Pb were best degraded at P2, while combined Zn were at P4.

Keywords: pollution, factory, biofilter combination, the heavy metals Cd Pb Zn, Gracillaria sp., Anadara granosa, Zeolite

1. Introduction

Heavy metal pollution is hazardous for the environment. Environmental pollution occurs due to the inclusion of organism, substances, energy and/or other components into environment and or due to changes of environmental order caused by human activities or natural process, leading the quality to decrease to a certain level, which cause the environment function to decrease or to stop (Sastrawijaya, 2000).

One of the heavy metals in waters that are poisonous for organisms is Lead (Pb) (Achmad, 2004). Highly concentrated heavy metal Pb in waters is able to kill aquatic biota. Pb concentration of 188 ppm can kill fish, while Crustacea will be killed when exposed to the concentration of 2.75-49 ppm after 245 hours (Palar, 2004). According to the Minister of Environment’s Decree No. 51 of 2004, seawater quality standard criteria on the heavy metal Pb for aquatic biota is 0.008 ppm. Cadmium (Cd) is one of the B3 (Hazardous Toxic Materials) waste that becomes one of the source of heavy metal pollution in seawaters.

Bivalves often function as the indicator of heavy metal pollution due to its ability to accumulate heavy metals from its surrounding, wide distribution, sedentary life and filter feeder nature (Mostafa et al., 2009). Gracillaria sp. is macroalga with high adaptability towards changes in water quality (Komarawidjaja, 2003). Zeolite is porous material with extensive uses. The use of zeolite is based on its abilities in ion exchange, adsorption, and catalysis (Ginting, 2007).
Biofilter is a system for wastewater management implemented by streaming the wastewater into a biological reactor filled with filter media to breed microorganisms that decompose contamination within the wastewater with or without aeration (Filliazati et al., 2013).

2. Material and methods

2.1. Time and place

This study was conducted on May 8-15, 2017 at the Faculty of Fisheries and Marine Universitas Airlangga Surabaya. Biofilter was prepared at the web laboratory of the Faculty of Fisheries and Marine Universitas Airlangga.

2.2. Tools and materials

The tools used were 20 aquariums with the size of 40 cm x 30 cm x 30 cm divided into 3, aerator, scales, water quality measuring device (thermometer, refractometer, pH meter and DO meter). The materials used were blood clamps (A. granosa) originated from the waters in Sedati region, Sidoarjo. The blood clams used were 15 grams in weight. Each aquarium had different combination of blood clamp and seaweed. Maintenance medium for the seaweeds and blood clamps was seawater with salinity of 25 ppt. Zeolites were also used in each treatment.

2.3. Research procedure

As the initial preparation prior to the use, the aquariums were washed with clean water and dried out. The clean-washed tools were soaked in chlorine solution of 150 mg/l for 12-24 hours. In order to dispel the chlorine odour and dirt, the aquariums were washed using detergent by scrubbing the walls and aeration hose which functions to kill parasite, and were rinsed with freshwater afterwards (Prakosa 2013).

The aquariums were then filled with 10 liters of seawater with salinity of 26 ppt. After that, aeration, water pump, nets, blood clamps, seaweeds and zeolites were installed in each aquarium.

The blood clams used were brought alive from the fishermen in the waters of Sedati, Sidoarjo. The blood clamps intended to be used as filters were acclimatized first before used as the experiment materials. The amount of blood clamps used were 600 g for 100% filter, 450 g for 75% filter, 300 g for 50% filter and 150 g for 25% filter. The density of the blood clamp was 600 g with aquarium size of 40 cm x 30 cm x 30 cm. According to FAO 2008 standard, blood clamp density used for small-scale maintenance media is 500 liters with maximum density of 30 kg.

The seaweeds used were Gracillaria sp., brought alive from a pond in Medokan Ayu area, Surabaya. The seaweeds intended to be used as filter were acclimatized first before used as experiment materials. The amount of seaweeds used were201 g for 100% filter, 158 g for 75% filter, 105 g for 50% filter and 53 g for 25% filter. The seaweeds were determined from the volume of water used. According to the previous study (Yulianto 2006), the stocking density of seaweeds used for filters is 500 gr in an aquarium with the size of 80 cm x 60 cm x 50 cm.

Five aquariums were used in this study, each containing a biofilter combination of blood clamp, seaweed and zeolite.

3. Results and discussion

Heavy metal pollution is hazardous for the environment. Environmental pollution occurs when organisms, substances, energy, or other components enters the environment, reducing its quality to a certain level and causing its function to decrease or stop (Sastrawijaya, 2000).

Biofilter is a system for wastewater management implemented by streaming the wastewater into a biological reactor filled with filter media to breed microorganisms that decompose contamination within the wastewater with or without aeration (Filliazati et al., 2013).
Figure 1. Reduction of heavy metals in fertilizer waste.

Description: P0 = 100% Seaweed (Gracilaria sp.) and Zeolite, P1 = 75% Seaweed (Gracilaria sp.), 25% Blood Clamp (Anadara granosa) and Zeolite, P2 = 50% Seaweed (Gracilaria sp.), 50% Blood Clamp (Anadara granosa) and Zeolite, P3 = 25% Seaweed (Gracilaria sp.), 75% Blood Clamp (Anadara granosa) and Zeolite, P4 = 100% Blood Clamp (Anadara granosa).

The test result of heavy metal content in water before using biofilter combination was 1.115 ppm. In the chart above, treatment P2 shows the best result with the content of 0.0736 ppm, followed by P4 with the content of 0.1900 ppm, P3 with the content of 0.2643 ppm and P1 in the last place with the content of 1.2630 ppm. The best biofilter combination based on the water lab test for Pb content was in treatment P2 (combination of 50% seaweed, 50% blood clamp and zeolite). The result of ANOVA test also indicates a significant effect in each given treatment. Seaweed and blood clamp were able to absorb the heavy metal Pb. This confirms that seaweed Gracilaria sp. has greater effect, because Komarawidjaja (2003) argued that Gracilaria sp. macroalgae with high adaptability towards changes in water quality. It enables Gracilaria to survive under the pollution of heavy metals with their growth rate remains undisturbed. As for blood clamps, their filter feeder attribute causes them to eat everything. Since heavy metals in waters are usually in the form of ion, the heavy metals were absorbed through the water that goes through their gill membranes or food. Beside through the gill, heavy metals also enter through skin (cuticle) and mucous layer, then lifted by blood, and might heap up in the clamps’ hearts and kidneys (Noviana, 1994).

Clamps possess the ability to accumulate heavy metals into their bodies, causing the content of heavy metals in the bodies to keep increasing so long as the clamps live in the waters contaminated with heavy metals. The content of heavy metals in the clamps’ body might even be higher than that of their surrounding (Hutagalung dan Razak 1981).

The test result for heavy metal cadmium (Cd) content in the water before treatment was 0.1058 ppm. Meanwhile, the test result after treatment showed that in P2 has 0.025 ppm, which is lower than P1 with 0.222 ppm; P0 with 0.0225 ppm; P4 with 0.0242 ppm and P3 with 0.0251 ppm. The different results indicate that biofilter combination can affect the reduction of heavy metal cadmium (Cd) in NPK fertilizer factory waste. The best biofilter combination based on the water lab test for the content of heavy metal cadmium (Cd) was in treatment P2 (combination of 50% seaweed, 50% blood clamp and Zeolite). The result of ANOVA test also implies that there was a significant effect in each treatment given to the factors Gracilaria sp. and Anadara sp. biofilters towards the reduction of heavy metal cadmium (Cd) concentration, p<0.05. Seaweeds and blood clamps are able to absorb...
heavy metal cadmium (Cd). The absorbability of *Gracillaria* sp. depends on the availability of toxic metals in the waters. Higher availability of toxic metal in the waters will spur high absorbability of *Gracillaria* sp. in the waters containing heavy metal cadmium (Cd). According to Phillips (1980), the entering of heavy metal element into plants’ bodies causes a compound between metal with protein and polysaccharide, which is then able to permeate cell walls and enter the cytoplasm.

Yulianto (2006) argued that *Gracillaria* sp. has a tolerance limit in coping with the condition of water contaminated with toxic metals. Continuous toxic metal absorption will lead to decreased absorbability as a result of decreased physiology function due to body metabolism impairment and a probability of damage in plant anatomy. Several symptoms are caused by the excessive toxic metals, such as cadmium (Cd), causing nutrient absorption process, which inhibit its life (Chino, 1981).

The result of research on the effectiveness of seaweed (*Gracillaria* sp.), blood clamp (*Anadara granosa*) and zeolite combination toward the reduction of heavy metal Zn in fertilizer factory waste shows that the most effective treatment was P4 with Zn content of 0.028 ppm and composition consisting of 100% blood clamp and zeolite. The second most effective treatment was P2 with Zn content of 0.029 ppm, followed by P3 with Zn content of 0.031 ppm and P1 with Zn content of 0.038 ppm. Meanwhile, P0 came out as the least effective treatment with Zn content of 0.060 ppm. It can be seen that the most effective combination in Figure 5.1 indicates that *A. granosa* has different ability in accumulating heavy metal Zn in NPK fertilizer waste.

This study’s result indicates that *A. granosa* accumulates Zn at around 1.29-2.44 ppm. The presumption is that the bigger the blood clamp’s size, the lower the Zn content will be. Amriani et al., (2011) clarified this by stating that very small or young blood clamps show higher accumulation ability compared to those that are bigger or older. Bigger or older clamps have a better ability in eliminating heavy metals.

| Parameter | P0 | P1 | P2 | P3 | P4 |
|-----------|----|----|----|----|----|
| DO (mg/L) | 3.7 | 3.2 | 2.7 | 1.8 | 1.8 |
| pH        | 7.5 | 7.5 | 7.5 | 7.5 | 7.5 |
| Salinity  | 26  | 26  | 26  | 26  | 26  |
| Temperature | 30.3 | 30.05 | 29.3 | 28.8 | 29.1 |

Description: pH = power of hydrogen, mg/L = miligram per liter

During the research, water quality was also observed as supporting variable (Table 1). Darmono (2001) argued that aquatic environmental factors that affect heavy metal toxicity are temperature, salinity, acidity (pH) and dissolved oxygen (DO). Those factors are used to determine the quality of waters (Afrianto and Liviawaty, 1998). The average temperature in the treatments was around 29.5°C, while the pH was around 7 and dissolved oxygen was 7.5. Water quality can be seen in Table 1. The observation on the water quality did not show any significant difference.

4. Conclusion
The result of this study shows that the use of biofilter combination can reduce the content of heavy metals Pb, Cd and Zn. However, there are differences in the effectiveness of biofilters in absorbing heavy metals. Pb and Cd are best absorbed in P2 combination, while Zn is best absorbed in P4 combination.

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