Enhancing removal efficiency of heavy metals and ammonia in bioretention system using quartz sand and zeolite as filter media

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Abstract. Bioretention is one of the stormwater runoff management systems to reduce pollutant concentration such as heavy metals and ammonia. However, removal efficiency of bioretention was affected by variation of filter media. So, the aims of this study are to enhance removal efficiency of bioretention system. Three bioretention system were applied on pilot scale sized 30 × 30 × 80 cm³ combined with Iris pseudacorus. Variation of filter media composition of quartz sand and zeolite was used with ratio 1:3, 1:1, 3:1, on reactor 1, 2 and 3, respectively. Synthetic runoff water with different concentration were simulated. The results shown that variations in influent concentrations has small effect on the removal efficiency (20-40%). The average removal efficiency of bioretention 1, 2 and 3 for Pb was 91%, 78%, 83%, respectively, followed 88%, 95%, 94% for Zn and 97%, 98%, 96% for NH₃. The combination of quartz sand and zeolite as filter media significantly enhance removal efficiency by 11.5% for NH₃, 18% Pb and 20% Zn compared to previous similar research.

1. Introduction
The phenomenon of urbanization around the world leads to an increase impervious surface areas such as roads, sidewalks and parking lots resulting in reduced natural infiltration into the soil [1] so increase the volume of storm water runoff. In stormwater runoff contained heavy metals including Cd, Pb, Ni, Cr, Zn [2] and nutrients which consists of nitrogen (TN, TKN, organic nitrogen, ammonia, nitrate, nitrite) and phosphorus. The presence of heavy metals in storm water runoff may result from tire fragments of automobiles and brake fluids, automotive liquid spills and copper deposits as anti-rust coatings, asphalt cuts, vehicle fumes and lubricating leaks [3]. While, for the source of nutrients in storm water runoff can come from human activities and natural processes. Several studies have suggested that the concentrations of heavy metals and nutrients in storm water runoff have exceeded the quality standards [3][4]. Concentrations of heavy metals and nutrients that have exceeded the quality standard require treatment to reduce or eliminate concentrations in stormwater runoff so as not to harm water bodies. One of the most efficient and often used types of LIDs is the bioretention [5].

The bioretention system is a landscape basin that receives runoff from uneven surfaces and consists of several layers of filter media and vegetation [5]. Field studies [6] and laboratory studies [7] suggest that bioretention is an efficient facility for removing heavy metals from stormwater runoff with...
removal efficiency > 90%. The pilot scale bioretention experiments in Texas also show that the ammonia (NH$_3$) removal in stormwater runoff with a of ± 20 minute is 87.7-95.6% [8]. One of contributing factor in removal efficiency of heavy metals and nutrient removal is filter media [6]. Filter media is a key factor in the design of bioretention [5]. The use of different filter media will result in different removal efficiency. Zeolite as filter media has the highest removal efficiency on Pb with 99% [9] and able to removal NH$_3$ until <0.1 mg/L [10]. For quartz sand, it effective to removal Pb with the removal efficiency until 71.38% [4]. Research on the effectiveness of the bioretention system to the filter media used has been widely applied [1][2]. In some of these studies only discuss the potential of each media in removing heavy metals in stormwater runoff, but only a few who examine the associated combining of several media and the proportion of media in the column bioretention, so it needs to do further research on the combination of filter media to removal pollutants, especially for the combination of quartz sand and zeolite.

For this reason, the purpose of this work is to analyze the influence of combination of filter media from quartz sand and zeolite to increase removal efficiency of Pb, Zn and NH$_3$ related to mass proportion. In this study, quartz sand and zeolite were combined with different percentages on three reactors and added with soil, compost and Iris pseudacorus as plant. All three reactors will be tested using synthetic runoff water with five different concentration.

2. Materials and Methods

2.1. Pre-Sampling

Stormwater runoff sampling was conducted at the field during two rainfall events. Sampling is carried out at several points which are adjusted to the runoff flow direction.

| Pollutant | Quality Standard (mg/L) | Runoff Sample 1st | Runoff Sample 2nd |
|-----------|-------------------------|-------------------|-------------------|
| Pb        | 0.03                    | 0.7257            | <0.00086          |
| Cu        | 0.02                    | < 0.005           | <0.00046          |
| Zn        | 0.05                    | 0.397             | 0.11              |
| Cd        | 0.01                    | < 0.00011         |                   |
| NH$_3$N   | 0.5                     | 2                 | 3.7               |
| NO$_3$    | 20                      | 15                | 28                |
| TP        | -                       | 8                 | -                 |

Based on Table 2, there are two heavy metals that exceed the quality standards based on Government Regulation No. 82 of 2001, that is Pb and Zn. So that these two parameters were selected as main pollutant. While for nutrients, ammonia is chosen as a pollutant to be used in synthetic runoff water.

2.2. Synthetic Runoff Water Preparation and Dosing

Synthetic runoff water is made with tap water mixed with heavy metal concentration as listed in Table 3. Previously, the tap water that would be used for synthetic runoff was dechlorinated first to remove residual chlorine, which is to silence tap water for 24 hours at room temperature to be sterile. Furthermore, the tap water is mixed with chemical solids Pb (NO$_3$)$_2$, ZnCl$_2$ and NH$_4$Cl so that synthetic runoff water produced a designed concentration. After mixing, the water is stirred to flatten the chemicals.

Table 3. Synthetic runoff concentration
2.3. Experimental Device

The experimental device consisted of a reservoir (300 liter), a submersible pump (Q=240 liter/minute), PVC pipe (L=±1.5m) for water distribution and three bioretention reactors. The structure of media layer, from top to bottom, consisted of 5 cm mulch, 5 cm compost, 5 cm soil, 40 cm filter media consist of quartz sand and zeolite with different mass of percentage. The drainage layer used 10 cm gravel layer (Figure.1). There was a geotextile layer between the media layer and the gravel layer to prevent zeolite or quartz sand penetrated into the gravel and made clogging.

2.4. Sampling Methods and Data Analysis

Experiments were carried out by five repetitions for each pollutant according to the concentration level presented in Table 3. The method used to determine the concentration of Pb and Zn in synthetic runoff is ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrophotometer) method. The detection limit of the ICP-EOS device was 0.86 ppb for Pb and 7 ppb for Zn. As for the parameter NH₃, concentration spectrophotometer DR-2000 with detection limit of 0.01 ppm was used. Removal efficiency of Pb, Zn and NH₃ concentration from each reactor was calculated using the following equation:

\[ Removal \, Efficiency \, (\%) = \frac{C_i - C_e}{C_i} \times 100\% \]

where \( C_i \) is total influent concentration of pollutant (mg/L) and \( C_e \) is total effluent concentration of pollutant (mg/L).

3. Results and Discussion

3.1. Removal Efficiency of Heavy Metals and Ammonia

Figure 2 shows the removal efficiency of Pb, Zn, and NH₃ from bioretention 1, 2, and 3 with five variations of influent concentration. Based on Figure 2a, it can be seen that the trend of removal efficiency tends to decreased up to the 4th running and increased at the 5th running. The declined of removal efficiency might be due to media in the bioretention has reached the saturation point, so that
the ability to remove Pb becomes lesser. This saturated condition causes the media pores to become smaller so that its ability to remove Pb decreases [11]. In addition, an increase in Pb effluent concentration can also be caused by the desorption process. Plants also contribute to the increase effluent concentrations through a detoxification process. On the other hand, the raise of removal efficiency in the last running can be caused by the desorption process which causes the adsorption site to increase, so that the removal efficiency increases. Plants also contribute to the increase in the percentage of removal at the 5th running, which is through the detoxification process [12]. In general, the results indicate that, although the media has performed well at low concentrations, filter media is still able to maintain high removal efficiency for experiments with greater influent concentrations [7].

Figure 2. Relation of concentration and removal efficiency of: (a) Pb; (b) Zn; and (c) NH₃

In the case of Zn removal efficiency, the largest percentage is dominated by bioretention 2 and the smallest percentage was found in bioretention 1 (Figure 2b). The trend of Zn removal is the same as Pb, when the concentration of influent increases, more adsorption sites are needed, so with increasing Zn influent concentration has shown the opposite effect on removal efficiency. In the 1st running, the removal efficiency of Pb was larger than Zn due to competition between heavy metals in occupying zeolite adsorption sites, which is available as a zeolite selectivity tendency for different cations. It was reported that Pb was the first pollutant with 67-88% of removal efficiency [13]. Analysis of equilibrium studies shows that Pb accumulation on large surfaces is available and more adsorption on the outer surface of zeolites. As a result, other heavy metal ions have a lower absorption compared to Pb. Based on Figure 2c, the ammonia concentration in all running is below the quality standard of 0.5 mg/L. The low ammonia effluent concentration at each running were followed with high removal efficiency, which was almost all over 90%. However, the trend ammonia removal efficiency data did not show stability, which continues to fluctuates from the initial to the end of running.

From the averaged of removal efficiency at each bioretention for each pollutant in Figure 2a, 2b and 2c, there is a difference in values reaching 13% for Pb, 7% for Zn, and the smallest is 5% for NH₃. To find out whether there are significant differences in the percentage of Pb, Zn and NH₃ removal in bioretention 1, 2 and 3 due to variants composition of filter media, a one-way ANOVA statistical analysis was performed. The three sig values (ρ) for each pollutant has a value of >0.05. It indicates that there is no significant difference between bioretention 1, 2 and 3. This might be due to the scale of experiment being applied was a pilot scale, with a small bioretention size so that the difference in the composition of filter media in each reactor was not significantly affect the removal rates of pollutant. Hence, it is possible that the percentage of removal efficiency will increase. Although based on ANOVA test there was no significant difference, but there was an increase in the efficiency of Pb, Zn and NH₃ compared to the previous similar research at the same study site (Figure 3).
The percentage of removal efficiency of Pb is compared with the research conducted by [4] which uses only one type of filter media (quartz sand). Bioretention planted with *Iris pseudacorus* and using quartz sand as filter media had a removal efficiency of 71.38% [4]. From this present research, there was an increase of ± 20% if composition variations such as bioretention 1 were carried out. For Zn, there was also an increase in removal efficiency, although the study sites were applied differently which used one type of filter media, with removal efficiency of Zn 77.04% [14]. When compared to this present research, there is an increase in the percentage of Zn removal efficiency of ± 18%. Meanwhile, for ammonia because there is no research in the same location, then as a comparison several studies are used [15]. From these studies, the averaged removal efficiency for ammonia is ± 86%. So, mix of media that has been done in the present research, shown an increase of removal ammonia by ± 11.5%.

### 3.2. Factor Affecting Removal Efficiency

#### 3.2.1. Influent Concentrations

Effect of influent concentration on the removal efficiency observed through a linear regression test, which can show the relationship between the dependent variable (removal efficiency) and the independent variable (influent concentration). The regression test shows that, influence of ammonia concentration has the greater effect (40%) than the others heavy metals (Pb and Zn) which has 20%. So, removal efficiency of ammonia and heavy metals was affected by other factors outside the experiment setting by 60% and 80%, respectively.

#### 3.2.2. Plant Types (*Iris pseudacorus*)

The roots of *Iris pseudacorus* in each bioretention revealed to have more Pb and Zn content than leaves (Figure 4). This is because the plant roots have an absorption capacity of 9-14 times greater than the leaves. The absorption and accumulation of heavy metals by plants is divided into 3 mutually sustainable stages, that is the absorption of metals by the roots, translocation of metals from roots to other parts of plants, and localization of metals in certain parts [16]. It can be interpreted that the root is the first recipient of heavy metal contained in synthetic runoff water, so that the most absorbed amount will be at the roots. From these data, a Pearson correlation statistical test was also performed to find out if there was a relation between the amount of heavy metal absorbed by the roots and leaves in plants. The test results show absorption of Pb and Zn by the roots and leaves have strong-enough relationship.
3.2.3. Filter Media

In this study, the pollutant concentration which might be absorbed by the filter media was not tested so the direct effect of the filter media on removal efficiency could not be reported. However, by employing simple life cycle analysis (mass balance) of the concentration contained in influent, effluent and plants, it can be estimated the amount of concentration absorbed by the filter media. It suggests that influent of heavy metals which were discharged into the bioretention system would approximately 12% was leave out as effluent, 18% absorbed by plants (3 Iris pseudacorus aged 3 months) and 70% remained in the filter media. Filter media have an important role in pollutant removal, which is mainly through the process of adsorption and ion exchange.

4. Conclusion

A combination of filter media using quartz sand and zeolite, was successfully increase removal efficiency, which increased by 20% for Pb, 18% for Zn and 11.5% for ammonia. The influent concentration has a small effect on the removal efficiency, which is around 40% for ammonia removal and around 20% for heavy metal (Pb and Zn). Overall, the influent concentration is inversely proportional to the percentage of the filter media receptivity, i.e. the greater influent concentration, will decrease the percentage of receptivity. In addition, the presence of Iris pseudacorus on bioretention systems contribute to about 18% in removing Pb and Zn, whereas plant roots have an absorption capacity of 9-14 times greater than the plants' leaves.

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