Impacts of zeolite activation temperature and grain size toward bioretention system efficiency in removing Pb and Zn pollutant in stormwater runoff

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Abstract. Stormwater runoff can be utilized as a clean water supply through a simple treatment technology such as a bioretention system. However, this water treatment efficiency is influenced by various factors. Previous research showed that although the bioretention system had combined with a plant and media composition, effluent concentration still exceeds the quality standard. This research aimed to improve the bioretention efficiency in removing heavy metal Pb and Zn in stormwater runoff. Three variations of bioretention were prepared, with the same combination of 2 types of plants (Chrysopogon zizanioides and Iris pseudacorus) and media composition (zeolite: quartz: compost: soil = 6:2:1:1). The zeolite activation temperatures and grain sizes simulated with three discharges variation of initial Pb and Zn concentration of synthetic stormwater runoff. The results showed that modified bioretention produced higher Pb removal efficiency (99.95% on average) and Zn (98.89% on average). Besides, the effluent concentrations have met the water quality standard following Government regulation No. 82/2001. In conclusion, the higher temperature of activated zeolite combined with smaller grain size significantly enhance the removal efficiency of Pb and Zn in stormwater runoff.

1. Introduction
The population growth causes changes in land use functions, thereby reducing the quantity of water absorbed into the soil, and increasing surface runoff resulted in flooding during the rainy season and drought during the dry season [1]. Rainwater runoff can have certain pollutants, such as Zn and Pb. Zn metal's primary source comes from rubber tires, fuel, oil, and brake pads, while Pb metal comes from the use of fuels containing lead [2]. Rainwater runoff on roads can have heavy metal concentrations: Pb as much as 56 μg/L to 774 μg/L and Zn as much as 1421 μg/L to 59.855 μg/L [3]. Heavy metals in water can accumulate in the organism for a long time as toxins [4].

One of the methods that can be applied to treat the rainwater runoff is bioretention. The bioretention system's ability to remove pollutants is satisfactory because it can remove up to 90% for suspended solids' total parameters, above 95% for heavy metals (Pb, Zn, and Cu) and high efficiency in removing other pollutants [5].

There have been several studies related to bioretention made by researchers from the Environmental Engineering University of Indonesia (2017,2018) that the effluent quality has not met the water quality standard class III according to Government regulation No. 82/2001 for Zn parameters (maximum
threshold value of 0.05 mg/L) and Pb (maximum threshold value of 0.03 mg/L) [6-8]. Further research is needed to improve the efficiency of the bioretention system to remove these pollutants.

The smaller the zeolite size, the higher its ability to adsorb the concentration of metal because the smaller zeolite has more absorbent pores [6]. Zeolites with relatively small pores contained many impurities that could cause interference with the reactants' diffusion process towards the active site of the catalyst if given no activation treatment or used directly [7].

Physical activation of zeolite is carried out by heating, so the contained water evaporates, and the size of the pores increases. It is acknowledged that the optimum zeolite porosity value is achieved with a heating temperature of 200°C. When heating is performed at temperatures above 200°C, the microstructure will become denser or smaller [8]. Based on research conducted by Rini and Antonius (2010), the higher the activation (heating) temperature, the more contained water in the zeolite crystal evaporates [9]. The water evaporation causes the pores of zeolite crystal to open and become broader so that the adsorption capacity increases.

This study aims to increase the bioretention system's efficiency in removing Pb and Zn to meet quality standards. Increasing the efficiency of bioretention is conducted by varying the combination of media, plant, and zeolite (simulated grain size and activation temperature).

2. Methodology

Three bioretention reactors were prepared with various treatment media (size and zeolite activation temperature), presented in table 1.

| Bioretention | Treatment of Zeolite |
|--------------|----------------------|
|              | Size (mm)            |
| A            | 1.19 - 2.38          |
| B            | 0.841 - 1.41         |
| C            | 0.841 - 1.41         |
|              | Activation Temperature (°C) |
| A            | 200                  |
| B            | 200                  |
| C            | 105                  |

Reactor A and B were observed to compare the effect of differences in grain size; meanwhile, reactor B and C were observed to compare the effect of differences in zeolite activation temperatures. The three bioretention reactors have a dimension of 33 × 33 × 80 cm³, equipped with *Iris pseudacorus* and *Chrysopogon zizanioides* plant, and media in the following order from the bottom to top: 60% zeolite, 20% quartz sand, 10% soil, and 10% compost. Figure 1 shows the bioretention system in the initial stage of the research.

![Figure 1. Pilot-scale bioretention reactor.](image)
Synthetic rainwater runoff prepared using a mixture of water, Pb(NO₃)₂, and ZnCl₂ with an initial concentration of Pb 0.44-1.03 mg/L and Zn 1.39-2.88 mg/L, referring to the initial effluent concentration that had not met the quality standards in research conducted by Sari [10]. Table 2 shows the variation in Pb and Zn concentrations in synthetic rainwater runoff for the three flows.

| Number of flows | Pb Concentration | Zn Concentration |
|-----------------|------------------|------------------|
| 1               | 0.44 mg/L        | 1.39 mg/L        |
| 2               | 0.51 mg/L        | 1.78 mg/L        |
| 3               | 1.03 mg/L        | 2.88 mg/L        |

A total of 9 samples collected from the outlet will be tested in the laboratory to analyze changes in lead and zinc metal concentration and compared with quality standards (Government regulation No. 82/2001). The t-test statistical analysis was used to determine the effect of differences in grain size and zeolite activation temperature on zinc and lead removal. Data from the laboratory were then processed and compared with the results of previous studies [6-8].

3. **Results and discussion**

The concentration of Pb in influent and effluent and the percentage of removal efficiency are presented in figure 2. The effluent concentration observed at the first, second, and third flow has the same value. (0,0003 mg/L). Due to the limited detection limit of the test equipment, the concentration <0,0003 mg/L could not be measured; therefore, the value measured is used to be analyzed.

![Figure 2. The Pb removal efficiency of the reactors.](image)

The decrease in Pb concentration from the three bioretention reactors was significant, indicated by a high percentage of removal (99.95% on average) to meet quality standards. This shows an improvement in the removal efficiency compared to similar previous studies [6-8]. Figure 3 shows the comparison of Pb concentration removal efficiency with several previous studies.

![Figure 3. Comparison of Pb concentration removal efficiency with several previous studies.](image)
The research conducted by Dwicahyani (2017) showed that the highest Pb removal percentage was 71.4%, where the bioretention reactor equipped with plants such as Iris pseudacorus and media consisted of quartz sand [11]. The research conducted by Agnes (2018) used a combination of filter media consisted of 60% quartz sand, 20% soil and 20% compost, and two types of plants: Iris pseudacorus and Chrysopogon zizanioides, resulted in the highest average percentage lead removal of 83.3% [12]. A combination of filter media of 60% zeolite (zeolite activation temperature 105°C and size > 2 mm), 20% quartz sand, 10% soil, and 10% compost, and 1 type of plant, Iris pseudacorus to produce the highest percentage of Pb removal of 91.2% [10]. The improvement of Pb removal efficiency in this study was due to smaller zeolite grain sizes, higher activation temperatures, and Chrysopogon zizanioides plants. Following the theory, the smaller the size of the adsorbent, the greater the active surface area. Hence the adsorption capacity increase [13]. Besides, the heating treatment can release the water bounded to the zeolite crystals. The higher the activation temperature, the more contained water will lose. Water will move towards the surface, then evaporate. Activation of zeolite by heating released contained water and caused the surface area of the zeolite pores to increase so that the adsorption ability increases [14].

Figure 4 shows the Zn concentration in influent and effluent and the percentage removal for the three flows. It observed clearly that the zinc concentration test results in the effluent can still be detected by the test equipment, except for the Zn concentration in reactor B during the second flow. As in the Pb concentration data in the effluent, for the Zn concentration value that the test instrument was not detected, the instrument detection limit value was used as a measured value, which was 0.001 mg/L.

In previous studies, the effluent Zn concentration did not meet the quality standard [6-8]. Whereas in this study, all Zn concentration in the effluent from the three bioretention reactors had met quality standards, applied if the maximum Zn concentration in influent is 2.88 mg/L. Figure 5 shows the average percentage of Zn removal in the three bioretention reactors.
Bioretention reactor B has an average percentage of Zn concentration removal of 99.27%. The bioretention reactor has the optimal Zn removal efficiency when compared to reactor A and C. The t-test results concluded that the difference in grain size and activation temperature did not significantly affect the removal of Pb and Zn. Comparison of removal efficiency with previous studies presented in figure 6 [6-8].

![Figure 6. Comparison of the percentage of Zn removal efficiency with previous research.](image)

Based on the research conducted by Sari [10], the highest average of Zn removal in bioretention was 94.7%. Meanwhile, in the research conducted by Agnes [12], the highest average of Zn removal in bioretention was 98.3%. The significant improvement in Zn removal efficiency in this study is potentially caused by the smaller zeolite grain size and the higher activation temperature.

4. Conclusion
Using smaller zeolite grain sizes and higher activation temperatures can significantly increase Pb and Zn removal efficiency in rainwater runoff. The bioretention reactor B used zeolite sizes from 0.841 mm to 1.41 mm, activated at 200ºC resulted in the best Zn removal efficiency, while no significant difference with bioretention reactors A and C displayed. Although there was no significant difference in Pb removal efficiency between bioretention reactors, the effluent has met the quality standards class III (Government regulation No. 82/2001 Class with a maximum Pb concentration of 1.03 mg/L and Zn of 2.88 mg/L.

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