Bio agent added organomineral nitrogen fertilizer for heavy metal contaminated paddy field treatment

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Abstract. Industrial waste in paddy field leads to accumulation of heavy metals in the soils. The availability of heavy metal on the soil can affect soil quality and plant growth. The objectives of this research were to obtain the best dosage of bio agent-added organomineral nitrogen fertilizer (ONF+BA) for the improvement of soil quality and paddy rice grown in industrial-waste contaminated soil. Randomized block design were applied with six single treatments: 150 kg ONF+BA (A), 200 kg ONF+BA (B), 250 kg ONF+BA (C), 300 kg ONF+BA (D), 350 kg ONF+BA (E), 250 kg urea (F), each treatment was replicated five times. The result showed that the application of ONF+BA reduced lead (Pb) and chrome (Cr) solubility and foliar accumulation, improved plant growth, and increase foliage nitrogen content. The doses of 300 kg ONF+BA shown highest lead and chrome solubility reduction, while 350 kg ONF+BA decrease foliar accumulation of lead and chrome.

1. Introduction
The existence of heavy metal on soil could certainly degrade soil quality and crop yield. These metals are potentially toxic for crops, animals, and humans, especially if the contaminated soils are used for crop production (Wong, et al., 2002). One of heavy metal sources on soil is from industrial waste. Release of wastewater from industry without proper treatment to the river as source of irrigation poses a significant threat to agricultural environment and ecosystem and accumulation on soil up to critical threshold. Heavy metals are non-biodegradable so its persistence, bio-magnification, and accumulation in food chain [1].

Rancaekek is a district that having a mass land conversion from agriculture into textile industrial area. According to [2] physical and chemical soil analysis in Rancaekek’s paddy fields showed the presence of pollutant such as Fe, Al, Cu, Zn, Pb, Co, Cr, and B. [3] stated that soils in Linggar village, Rancaekek sub-division contained 78,06 ppm of Cr which is classified as critical category. [4] stated that critical limit of Cr and Pb on soil is 2.5 and 100 ppm, respectively. Therefore, some efforts to reduce the availability of Pb and Cr on paddy field in Rancaekek are necessary.

The presence of heavy metal in soil are divide in two forms that is mobile (soluble) and immobile (unsoluble) form. Heavy metal on soil were accumulated in sediments and classified into five categories, there are adsorptive and exchangeable (ions), bound to reducible phases (Pb and Cr oxides), bound to carbonate phases, bound to organic matter and sulphides, and detrital or lattice metals. Heavy metal in soluble form (ions) can be absorbed by plants and affected plant growth and also yield quality. The solubility of heavy metal in soils depends mainly on soil chemical properties such as pH [5], CEC and

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redox Heavy metal in soluble form should be threatned into un-soluble or immobilization form so that it cannot be absorbed by plant.

The solubility of heavy metals in contaminated soil can be decreased by application of ameliorant. Ameliorant is a soil enhancer that can chelate heavy metals in the soils by reducing their solubility. The use of ameliorant or organomineral materials such as zeolite, activated charcoal, and organic matters has a potency to chelate heavy metals [6]. However, this effort could be more effective by utilizing potential microorganisms that have been evaluated to degrade heavy metal or toxic material such as bacterial. Pseudomonas fluorescens was the one of bacterial that could reduce of CrO$_4^{2-}$ to Cr (OH)$_3$ by redox reactions which involving enzymatic microbial detoxification of harmful metals or metalloids [7]. In order to assess the effectivity of ameliorant/organomineral and bioagent in absorbing heavy metal, the application of various organomineral and microorganism material will be conducted in this research. We hypothesize that these materials could binding the heavy metals and reduce the contaminant levels in soils.

Bio agent-added organomineral nitrogen fertilizer is a fertilizer product consists of urea, zeolite, coconut shell of activated charcoal, and compost with biological agent (Pseudomonas cepacia and Bacillus subtilis). These mixed materials function as slow released fertilizer which is able to degrade dangerous toxic materials, such as heavy metals in the soils. The purpose of this research is to produce a fertilizer product which is able to provide nutrients for the crops as well as to improve the quality of contaminated soils from heavy metals, especially on paddy fields.

2. Materials and Methods

2.1. Materials

The materials used in this research include: paddy fields from Rancaekek, Bio agent-added organomineral nitrogen fertilizer (ONF+BA) comprised urea, zeolite, and coconut shell of activated charcoal, compost with biological agent (Pseudomonas cepacia and Bacillus subtilis). Supporting tools in this research were: field equipment (bucket, scissors, sack, shovel, differentiator in each treatment and replication, gauge, stationery, label, ruler and weight), fertilizer machine, mixer, and laboratory equipment used in soil chemical analysis.

2.2. Methods

The experiment started from November 2017 to April 2018. The Bio agent-added organomineral nitrogen fertilizer (ONF+BA) consisted of 60% urea, 20% zeolite, 10% activated charcoal, and 10% compost with biological agent. The experimental design used was single factor Randomized Block Design (RBD). Experiments were performed by testing various doses of fertilizer consisting of six treatments; A = 150 kg ONF+BA, B = 200 kg ONF+BA, C = 250 kg ONF+BA, D = 300 kg ONF+BA, E = 350 kg ONF+B, F = 250 kg urea, each treatment was replicated five times. The average difference of treatment’s effect was tested to several observed parameters, such as nitrogen (N) availability, chrome (Cr) solubility, lead (Pb) solubility, Cr uptake, and Pb uptake at 60 days after fertilizer application. Furthermore, the tests were done by F test at 5% level. If the difference in mean treatment effect was real then the test was continued by Tukey's standardised range (HSD). Application of ONF+BA fertilizer conducted on moist soil condition. The bio agent-added organomineral nitrogen fertilizer given by being immersed in the soil with dept 3-4 cm from the surface of soil.

3. Results and Discussion

3.1. Soil acidity (pH)

Potential Hydrogen (pH) is an important factor in determining the soil chemical properties. Soil pH is one of the most determinant factors affecting metal solubility, plant nutrient uptake and movement and many other attributes and reactions in the soil [8]. Soil acidification increases heavy metal solubility in the soil [9]. In this research, soil pH was measured to know ONF+BA fertilizer effect to the soil. The effect of ONF+BA fertilizer towards soil pH on 60 days after application was shown on Table 1.
Based on analysis of variance, the application of various bio agent added organomineral nitrogen fertilizer showed significant effect toward soil pH at 60 days after application if compared with 250 kg ha\(^{-1}\) of Urea fertilizer. The lowest soil pH was showed by treatment of Urea application with 250 kg ha\(^{-1}\) doses.

**Table 1.** The average of soil acidity on 60 days after application.

| Symbol | Treatment          | Soil pH |
|--------|--------------------|---------|
| A      | 150 kg ha\(^{-1}\) ONF + BA | 5.06 b  |
| B      | 200 kg ha\(^{-1}\) ONF + BA  | 5.12 b  |
| C      | 250 kg ha\(^{-1}\) ONF + BA  | 5.20 b  |
| D      | 300 kg ha\(^{-1}\) ONF + BA  | 5.38 b  |
| E      | 350 kg ha\(^{-1}\) ONF + BA  | 5.11 b  |
| F      | 250 kg ha\(^{-1}\) Urea    | 4.53 a  |

*The numbers followed by the same letter are not significantly different based on Multiple Range Test Duncan at 5% level.

The application of various ONF +BA fertilizer not significantly different to soil pH in each treatment. Based on soil analysis, contaminated soil in Rancaekek has a soil pH of 4.6 which is classified as acid criteria. The application of various dose ONF +BA could increase soil pH up to 11.7 – 18.8 % from initial condition to be 5.06 – 5.38. Bio agent added Organomineral Nitrogen fertilizer were made by mixtures of several ameliorants such as zeolite, activated charcoal, and compost, so it has ability to increase soil pH. The used of compost could increase soil pH and have the ability to buffer soil pH.

Zeolite is the one of ameliorant which is had a high CEC so that could suppress de-nitrification process and also keep balancing of soil pH. The Treatment of 250 kg ha\(^{-1}\) Urea fertilizer application has affecting the decrease of soil pH from 4.6 to be 4.53. It was happened because application Urea into soil affecting nitrification process which could change ammonium into nitrate and produce of H\(^+\) ion. At low soil pH condition, heavy metal bioavailability increases due to its free ionic species (Pb\(^{2+}\) and Cr\(^{3+}\)) and in contrast, high soil pH decreases due to insoluble metal mineral phosphate and sulphide formation.

### 3.2. Heavy metal solubility on the soil

Heavy metals are accumulated in the soil. Lead is an element that cannot be degraded and destroyed in the soil. Leads could be soluble in the soil if in acid condition. Liming is one of methods to reduce heavy metal solubility (Pb and Cr) and metal absorption by plant. That is due to lead will be precipitated as phosphate hydroxide and carbonate. The concentration of Pb in agriculture ecosystem in range of 2 – 200 ppm. Heavy metal form in the soil which could be dangerous to plant and human life that is in soluble form. The soluble metal could be absorbed by plants directly. The average of lead and chrome solubility in the soil was shown on the table below:

**Table 2.** The average of heavy metal solubility on the soil.

| Symbol | Treatment          | Lead Solubility (ppm) | Chrome Solubility (ppm) |
|--------|--------------------|-----------------------|-------------------------|
| A      | 150 kg ha\(^{-1}\) ONF + BA | 1.10 a    | 1.86 d  |
| B      | 200 kg ha\(^{-1}\) ONF + BA  | 1.35 bc   | 1.83 d  |
| C      | 250 kg ha\(^{-1}\) ONF + BA  | 1.36 bc   | 1.03 b  |
| D      | 300 kg ha\(^{-1}\) ONF + BA  | 1.08 a    | 0.76 a  |
| E      | 350 kg ha\(^{-1}\) ONF + BA  | 1.14 ab   | 1.50 c  |
| F      | 250 kg ha\(^{-1}\) Urea    | 1.42 c    | 2.02 e  |

* The numbers followed by the same letter are not significantly different based on Multiple Range Test Duncan at 5% level.
Based on Table 2, there is a dose of fertilizer which has an effect on reducing the solubility of Pb in the soil at 60 DAA. Treatment of 250 kg ha\(^{-1}\) Urea fertilizer showed the highest Pb solubility at 60 DAA with Pb content of 1.42 ppm, but not significantly different with treatment of 200 kg ha\(^{-1}\) and 250 kg ha\(^{-1}\) ONF+BA fertilizer which had Pb content amounting to 1.35 and 1.36 ppm. The application of ONF+BA fertilizer at a dose of 300 kg ha\(^{-1}\) showed the lowest Pb solubility on the soil with a Pb value of 1.08 ppm, but not significantly different with a dose of 150 and 350 kg fertilizer ha\(^{-1}\) ONF+BA fertilizer.

Adsorption of heavy metal ionic form by ameliorant in soil solution could decrease heavy metal solubility. Lead soluble form in soil solution like Pb\(^{2+}\) could be adsorbed directly by ONF+BA fertilizer because of ameliorant mixture on fertilizer material. Bio agent added organomineral fertilizer contain ameliorant like zeolite, activated charcoal, and compost that adsorbed cation (cation base, metal) in soil solution. Activated charcoal was known that can used as the remediation material of heavy metal in the soil, depends on soil pH. Activated charcoal effective to adsorbed metal on acid condition (3.5 – 4.5) and decrease if the soil pH up to 6-7.

Table 2 shown the solubility of Cr metal in soil at 60 days after application of fertilizer treatment. Based on the analysis of variance, the treatment of various doses of ONF + BA fertilizer showed a significant difference when compared with the use of Urea fertilizer with a dose of 250 kg ha\(^{-1}\) to the solubility of Cr metal soil. The lowest Cr concentration was shown on treatment of ONF + BA fertilizer with a dose of 300 kg ha\(^{-1}\). Urea fertilizer treatment with a dose of 250 kg ha\(^{-1}\) shown the highest Cr metal concentration compared to other treatments. Chromium(III) mobility is decreased by adsorption to clays and oxide minerals below pH 5 and low solubility above pH 5 due to the formation of Cr(OH)\(_3\)(s) [111]. Chromium mobility depends on sorption characteristics of the soil, including clay content, iron oxide content, and the amount of organic matter present. Chromium can be transported by surface runoff to surface waters in its soluble or precipitated form. Soluble and un-adsorbed chromium complexes can leach from soil into groundwater. The leachability of Cr(VI) increases as soil pH increases. Most of Cr released into natural waters is particle associated, however, and is ultimately deposited into the sediment [12].

3.3. Heavy metal absorption on the plant
Based on Table 3 there are ONF+BA treatments that significantly affect Pb absorption on plants. ONF+BA treatment with a dose of 350 kg ha\(^{-1}\) shown the lowest lead absorption value amongst the others and significantly different on Duncan MRT’s test on 5% level. Heavy metal can be absorbed by plant if in soluble or mobile condition on the soil. Based on [13] Pb could absorbed by plant on the soil when the condition of soil fertility was getting low, in the other hand soil pH and CEC could be affecting metal solubility too. The use of ONF + BA could decrease Pb absorption by plant because its material contains of the fertilizer. The application of 350 kg ha\(^{-1}\) ONF + BA was the best treatment to decrease Pb Absorption on the plant.

Table 3. The average of heavy metal absorption on the plant.

| Symbol | Treatment       | Lead Absorption (ppm) | Chrome Absorption |
|--------|----------------|-----------------------|------------------|
| A      | 150 kg ha\(^{-1}\) ONF + BA | 0.13 b            | 0.20 b          |
| B      | 200 kg ha\(^{-1}\) ONF + BA | 0.12 b            | 0.19 b          |
| C      | 250 kg ha\(^{-1}\) ONF + BA | 0.11 b            | 0.15 b          |
| D      | 300 kg ha\(^{-1}\) ONF + BA | 0.12 b            | 0.17 b          |
| E      | 350 kg ha\(^{-1}\) ONF + BA | 0.08 a            | 0.11 a          |
| F      | 250 kg ha\(^{-1}\) Urea    | 0.15 b            | 0.23 b          |

* The numbers followed by the same letter are not significantly different based on Multiple Range Test Duncan at 5% level.
The result of analysis of variance in Table 3 showed that there is an ONF+BA dose treatment that significantly reduce plant’s Cr absorption. ONF+BA application with dose of 350 kg ha$^{-1}$ showed the lowest chrome absorption on plants compared to others and significantly different on Duncan MRT’s test at 5% level. This shows that the higher ONF + BA in treatment increases its ability to adsorb Pb. This is caused by the active charcoal and zeolite contains on that’s mixture. Based on [14] the activated carbon had high adsorbent surface area and it can remove metal ion like Pb from their respective solution system. There was some factors which affecting heavy metal concentration in the plant, that were heavy metal concentration in soil solution, heavy metal ions mobilization to root zone, heavy metal movement from root surface area into plant roots, and heavy metal movement in other plant tissue. The combination of active charcoal, zeolite, and biological agent in compost directly decrease Cr solubility on the soil so it could decrease Cr absorption by plant.

4. Conclusion
This research shows that there is an influence from various doses of Bio agent added organomineral nitrogen fertilizer to pH, heavy metal (Pb and Cr) solubility in the soils, and Heavy metal (Pb and Cr) absorption in the plant. Bio agent added organomineral nitrogen fertilizer have better result on improving soil properties such as pH, and also decreasing Pb and Cr solubility in soils and plant absorption than urea-based treatment which observed at 60 days after application. The doses of 300 kg ONF+BA shown highest lead and chrome solubility reduction, while 350 kg ONF+BA decrease foliar accumulation of lead and chrome.

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