



EDTA, Water-extractable Lead and Bioavailability of Lead in Non-mined Soil, Capped and Uncapped Tailings: The Effect of Biochar Amendment

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

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ABSTRACT

A study was undertaken to determine the effects of corn cob biochar application on Pb-water and Pb-EDTA extractable, pH and bioavailability of Pb in non-mined soil and mine tailings. Biochar was applied to soil/tailings at a rate of 0–8 t ha⁻¹ and incubated at room temperature for 4 – 12 weeks. Lettuce (*Lactuca sativa*) was planted on biochar-amended soil/tailings for 12 weeks. The levels of Pb in amended soil/tailings and lettuce were monitored after 0, 4, 8 and 12 weeks from incubation. The application of biochar decreased significantly the levels of EDTA-extractable Pb by 13–14%, 7–16% and 9 – 11% in non-mined soil, capped and uncapped tailings respectively after 12 weeks biochar application. Water extractable Pb concentrations also decreased by 30 – 33% in non-mined soil, 33 – 37% in capped tailings and 13 – 18% in uncapped tailings. The concentration of Pb in lettuce cropped on biochar-amended non-mined soil (0.2 mg kg⁻¹) and capped tailings (0.2 mg kg⁻¹) were within the maximum limit (0.3 mg kg⁻¹) in vegetable, while the amended uncapped tailings recorded Pb level (0.85 mg kg⁻¹) which is well above the permissible limit.

Keywords: *Corn cob biochar; water-extractable lead; EDTA-extractable lead.*

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1. INTRODUCTION

Soil pollution of trace elements such as lead (Pb) in soils is a major environmental problem that could be caused by waste dumping, abandoned industrial activities and incidental accumulation [1,2]. Several industrial sites have metal concentrations that exceed acceptable levels and are therefore a potential health risk for humans, animals and plants [3,4]. Lead pollution due to industrial activities can result in toxic effects such as skin and bladder cancers and also renal damage [5,6]. The application of biochar is increasingly becoming a sustainable technology that leads to the improvement of highly weathered and degraded tropical soils [7]. The application of black carbon, which exists in its charcoal form as biochar [8], improves soil physical and chemical characteristics such as bulk density, water holding capacity, permeability, nutrient retention and availability [9,7].

The hazards of heavy metals to the environment can be reduced by fixation in the soil, thereby decreasing bioavailability and further mobility [10]. Several research findings have been published on the use of zeolite, beringite and organic matter to immobilise metals through cation exchange, sorption, complexation and precipitation [11,12,13]. In contrast to the widespread publications on the use of zeolite, beringite and organic matter in the immobilisation of metals, limited literature is reported on the use of biochar to reduce metal mobility.

There is the need for the determination of the bioavailability of heavy metals in soils after remediation. The lettuce plant accumulates heavy metals in its aerial parts and could be used to assess the bioavailability of heavy metals remediated soils [14]. The bioavailability and mobility of metals is important in assessing the potential health risk to the population because of

the integration of metals in the food chain [15]. The specific objectives of this study were therefore to assess the effect of corn cob biochar on the:

1. Extent of alkalization of non-mined soil, capped and uncapped tailings.
2. Concentrations of Pb in amended non-mined soil/tailing and bioavailability of Pb in amended soil/tailings using lettuce as the indicator crop.

2. MATERIALS AND METHODS

Soils/tailings were sampled at the Obuasi Gold Mine Obuasi, Ghana. The site had non-mined soils and reclaimed tailings (capped and uncapped). Top soil/tailings samples (0-15 cm) were collected. Tables 1 and 2 present physical and chemical properties of the soil/tailings.

2.1 Soil Amendment and Incubation Experiment

The soil/tailings samples from the field were spread on brown paper and allowed to air dry at room temperature for 5 days. The air-dry samples were passed through a 2-mm nylon sieve to have fine earth fraction which was used for the amendment and incubation experiment. Five hundred (500) grams of air-dry fine earth soil/tailings samples were placed in plastic containers. The soil/tailings were amended with biochar at the rates of 0, 2, 4 and 8t ha⁻¹ (w/w) and then moistened to 60% field capacity. The completely randomised design with three replications was used. The samples were placed in the laboratory at a mean room temperature of 25°C and moistened weekly to maintain the soil at 60% field capacity. The amended soils/tailings were sampled at 0, 4, 8 and 12 weeks after amendment. Five random sub-samples were taken from each container and bulked for analysis at each sampling interval.

Table 1. Physical properties of soil/tailing at 0-15 cm depth

Soil property	Site			
	Non- mined soil	Capped tailings I	Capped tailings II	Uncapped tailings
Bulk density (g cm ⁻³)	1.26	1.33	1.32	1.39
Total porosity (%)	52.45	49.81	50.19	47.54
Soil texture				
Sand (%)	43.65	48.93	73.64	34.62
Silt (%)	46.34	41.06	24.35	61.37
Clay (%)	10.01	10.01	2.01	4.01

Table 2. Chemical properties of soil/tailings at the 0-15-cm depth

Soil property	Site			
	Non- mined soil	Capped tailings I	Capped tailings II	Uncapped tailings
Organic carbon (%)	2.13	0.63	0.55	1.02
Total N (%)	0.19	0.06	0.06	0.10
C: N ratio	11.21	10.50	9.16	10.20
pH (1: 2.5 - soil:water)	5.10	6.79	6.70	7.22
Extractable P - Bray I (mg kg ⁻¹)	6.58	16.57	4.17	1.53
Exchangeable cations (cmol_c kg⁻¹)				
Ca ²⁺	3.47	11.75	10.15	15.39
Mg ²⁺	1.60	8.54	3.47	9.61
K ⁺	0.21	0.42	0.41	1.40
Na ⁺	0.13	0.42	0.38	1.67
Total exchangeable bases (cmol _c kg ⁻¹)	5.41	21.13	14.41	28.07
Exchangeable acidity (cmol _c kg ⁻¹)	0.35	0.10	0.10	0.05
Effective cation exchange capacity (cmol _c kg ⁻¹)	5.76	21.23	14.51	28.12

2.2 Extraction of EDTA-Pb

The ammonium tetrasodium-ethylene-diamine-tetraacetic acid (Na₄-NH₄-EDTA) extraction procedure of Agricultural Development and Advisory Services (ADAS) was used [16,17]. Briefly, it involved weighing ten grams of air-dried soil/tailing into a clean, nitric-washed mortar the soil/tailing and then pulverised with a pestle. The pulverised sample was transferred into a 100 ml conical flask and 50 ml of 0.05 M (Na₄-NH₄-EDTA) (pH 7) was added. The flask with the soil: Na₄-NH₄-EDTA suspension was shaken at room temperature on a mechanical shaker at 125 rpm for 1 hr [16,17]. The slurry was then passed through a Whatman No 42 filter paper into a sterile 100 ml conical flask. The filtrate was brought to exactly 100 ml with the extraction solution. The Pb content in filtrate was analyzed using the Atomic Absorption Spectrophotometer (AAS, Spectr AA 220). The concentrations of Pb were then measured at a wavelength of 283.3 nm.

2.3 Extraction of Water Soluble Pb

Water soluble Pb was determined by weighing 5 g of soil sample into centrifuge tube and 50 ml of distilled water was added. The tube was capped and shaken in a mechanical shaker for 30 minutes. After shaking the content of the tube was filtered with Whatman no.42 filter paper. Lead level in the extract was determined by AAS at a wavelength of 283.3 nm.

2.4 Bioavailability Experiment and Plant Analysis

Bioavailability of Pb in the amended soils/tailings was determined in a second experiment. Biochar was applied at the rate 0-8 t ha⁻¹ and incubated for 12 weeks after which lettuce (*Lactuca sativa*) seedlings were planted. Lettuce was used as the indicator plant of the bioavailability of Pb due to its ability to accumulate high level of the metal [14]. The field practices for the cultivation of lettuce as described by [18] were followed. The aerial part of the lettuce plant was harvested 6 weeks after transplanting. The harvested plant was then washed in sequence in detergent solution, dilute 0.1 M HCl and distilled water. Moisture was wiped off the fresh shoot which was put in a paper bag. The plant sample was dried in an oven at 70°C to constant weight. The plant sample was homogenised using mortar and pestle. After grinding, the sample was placed in a desiccator before sampling for Pb analysis. A quantity of 1.0 g of the prepared plant material was digested in freshly prepared mixture of HNO₃ -HCl (1:3 v/v) on a digester at 110°C for 3 h to determine the concentration of Pb [19].

2.5 Data Analysis

The Genstat statistical package [20] was used for the analysis the data. The analysis of variance (ANOVA) was used to determine the effects of the different rates of application of biochar on pH, water-soluble and EDTA-extractable Pb in the non-mined soil, capped and uncapped tailings.

The effects of the different rates of application of biochar on the bioavailability of Pb were also established using the ANOVA. The least significant difference (LSD) was used for the separation of means (95% confidence level).

3. RESULTS AND DISCUSSION

3.1 Biochar Effects on the pH of Non-mined Soil, Capped and Uncapped Tailings

The pH values ranged from 5.3 to 7.2 in un-amended soil/tailings (Figs. 1–3). The pH of amended soil/tailings increased with increasing rate of biochar application at 4 weeks after incubation (WAI). Thereafter, at 8 and 12 WAI, the increases in pH were successively lower with increasing rate of biochar application. Generally, at the end of the incubation period the increase in pH in amended soil/tailings ranged from 0.2 to 0.4 at the 8 t ha⁻¹ rate of application of biochar. Similarly, [21] obtained a pH increase of 0.4 in soil amended with char.

The different rates of application of biochar at 2, 4 and 8 t ha⁻¹ each resulted in significantly greater soil/ tailings pH compared to the control (0 t ha⁻¹) (at P= 0.05) at all the time-points of the incubation period (Figs. 1, 2 and 3). The highest soil pH was produced when 8 t ha⁻¹ of biochar was applied to the soil /tailings. However, the 4 and 8 t ha⁻¹ rates of application of biochar resulted in significantly similar pH values in uncapped tailings (Figs. 1, 2 and 3). The pH value of 9.35 (± 0.07) of the biochar applied was greater than the pH of 5.3 (± 0.0), 6.45 (± 0.07) and 7.2 (± 0.0) for un-amended non-mined soil, capped and uncapped tailings, respectively. This could have contributed to the alkalization of soil/ tailings through the neutralisation of H⁺ ions by OH⁻ ions derived from the formation of carboxyl, carbonyl and phenolic groups in the biochar structure [22,23]. The increased pH observed in biochar-amended soil/tailings has implications on heavy metal remediation. This is because the concentration of cationic metals such as Pb in soil solution decreases with increasing alkalinity [12,24].

3.2 Biochar Effects on EDTA- extractable Pb of Non- mined Soil, Capped and Uncapped Tailings

The different rates of application of biochar at 2, 4 and 8 t ha⁻¹ each led to significantly lower concentrations of EDTA-Pb compared to the

control (0 t ha⁻¹) in non-mined soil, capped and uncapped tailings (Figs. 4, 5 and 6).

At the end of the incubation period at 12 WAI, 4 t ha⁻¹ and 8 t ha⁻¹ of biochar resulted in significantly different concentrations of EDTA-Pb in non-mined soil (Fig. 4). However, each of these rates of biochar application resulted in significantly lower concentration of EDTA-extractable Pb than that of the control at 12 WAI (Fig. 4).

The concentration of EDTA-extractable Pb was significantly lower than that of un-amended soil/tailings (Figs. 4–6) possibly due to the increase in the pH of biochar-amended soil/tailings (Figs. 1–3) and subsequent retention and immobilization of Pb. Similarly, [25] noted that the adsorption of cationic metals increases with increasing pH. Secondly, the significantly lower concentrations of EDTA-extractable Pb in amended soil/tailings could also be attributed to the high specific surface area, charge density and negative surface charge possessed by biochar that result in a very high sorption and retention capacity of exchangeable cations [26].

3.3 Biochar Effects on Water Soluble Pb of Non-mined Soil, Capped and Uncapped Tailings

The results of the effects of biochar on water soluble Pb in non-mined soil, capped and uncapped tailings are presented in Figs. 7, 8 and 9. In the non-mined soil, there was no significant difference in the level of water soluble lead between the 4 and 8 t ha⁻¹ rates of application of biochar at 4 and 8 WAI (Fig. 7). However, the application of either 4 t ha⁻¹ or 8 t ha⁻¹ of biochar in non-mined soil resulted in significantly lower concentrations of water soluble lead at 12 WAI compared to the control (Fig. 7).

The significantly lower concentrations of water soluble lead (Figs. 7, 8 and 9) could be related to the corresponding significantly lower concentrations of EDTA-extractable Pb (Figs. 4-6) in biochar-amended soil/tailings. The decreased concentration of Pb extracted with EDTA implied that there was an increase in the residual fraction of Pb as a result of increased immobilization of lead. The increased pH of biochar amended soil/tailings compared to un-amended samples (Figs. 1-3) might have also contributed to the significantly lower levels of water soluble lead (Figs. 7–9) compared to the un-amended samples. This assertion is

confirmed by [12] and [24] who report that the concentration cationic metals such as Pb in soil solution decreases with increasing alkalinity. The oxidation of black carbon does not only increase its mineralization but also creates negative

charges that subsequently lead to greater CEC and nutrient retention in the soil [9]. This could also explain the significantly lower concentrations of water soluble lead in biochar amended non-mined soil, capped and uncapped tailings.

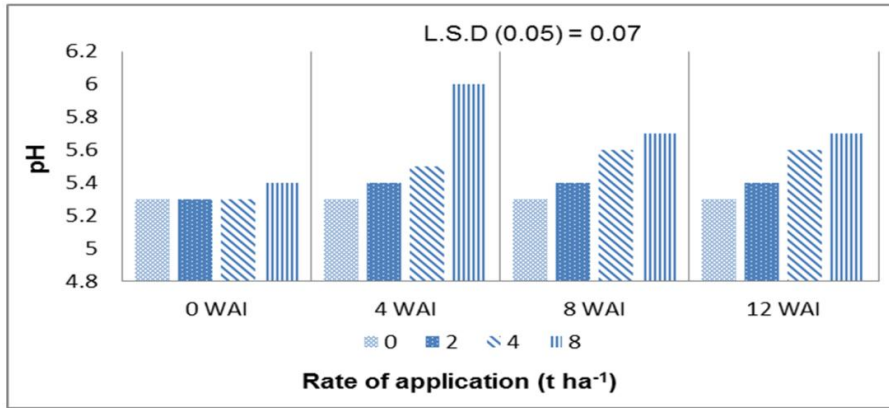


Fig. 1. Effects corn cob biochar on the pH of non-mined soil

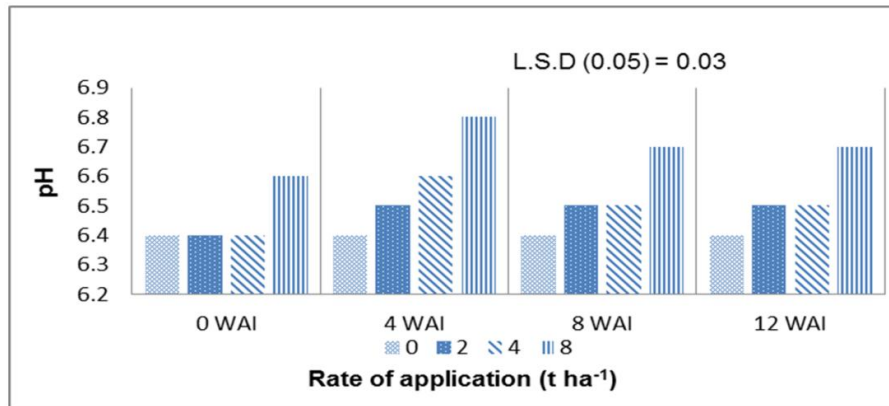


Fig. 2. Effects of corn cob biochar on the pH of capped tailings

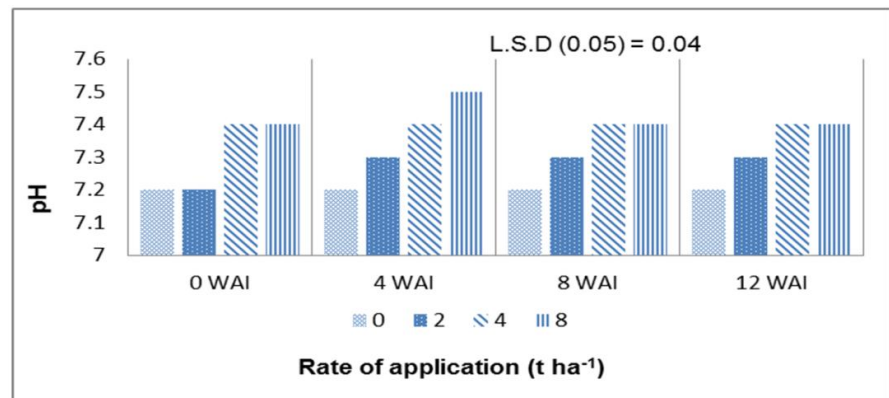


Fig. 3. Effects of corn cob biochar on the pH of uncapped tailings

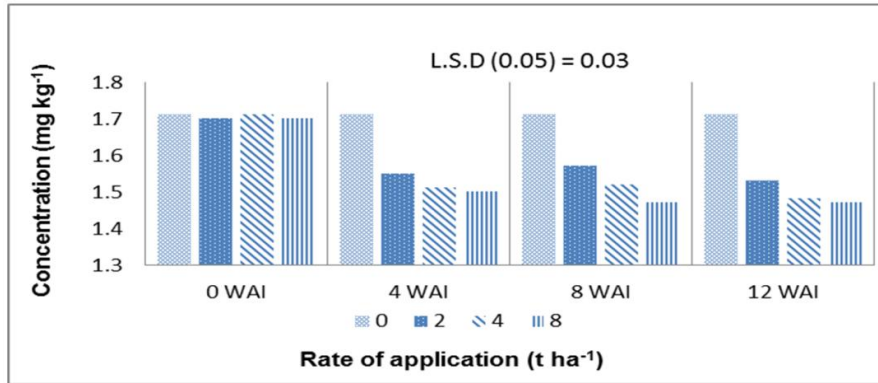


Fig. 4. Effects of corn cob biochar on EDTA-extractable lead of non-mined soil

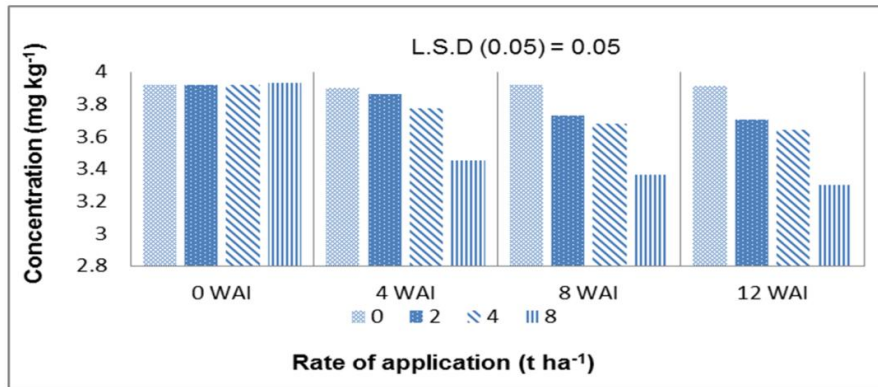


Fig. 5. Effects of corn cob biochar on EDTA-extractable lead of capped tailings

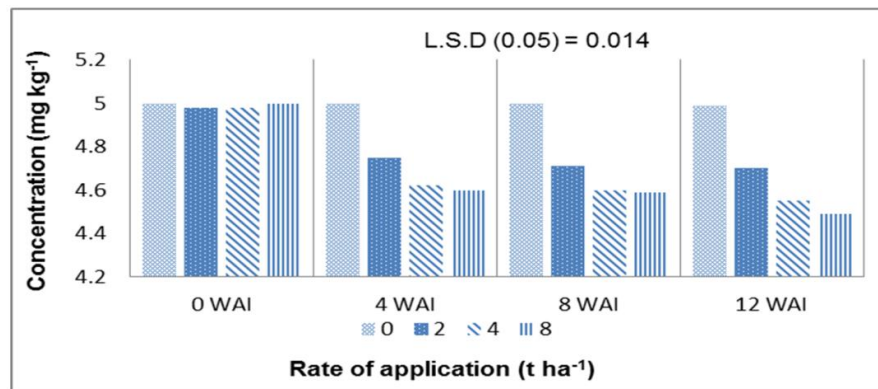


Fig. 6. Effects of corn cob biochar on EDTA-extractable lead of uncapped tailings

3.4 Biochar Effects on the Concentration of Lead in Lettuce Grown on Non-mined Soil, Capped Tailing and Uncapped Tailings

A steady decrease in the concentration of Pb in lettuce was observed with successive increases

in the rate of application of biochar in non-mined soil, capped tailing and uncapped tailings (Fig. 10). The reduction in the concentration of water soluble lead of biochar-amended soil/tailings with successive increases in the rate of application (Figs. 7 – 9) might have contributed to the corresponding lower concentrations of Pb in lettuce.

The pH of the biochar applied (9.35 ± 0.07) was greater than the pH values of un-amended soil/tailings. This could have contributed to the alkalization of non-mined soil, capped and uncapped tailings (Figs. 1-3). The increased pH observed in biochar-amended soil/tailings

possibly led to a reduction in the concentration of Pb in soil solution as observed by [12] and [24]. This subsequently resulted in a significantly lower level of Pb in lettuce grown on amended soil/tailings compared to un-amended samples (Fig. 10).

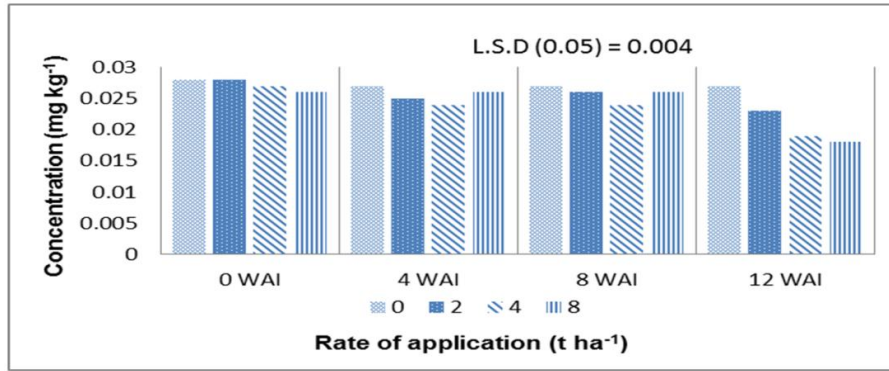


Fig. 7. Effects of corn cob biochar on water soluble lead of non-mined soil

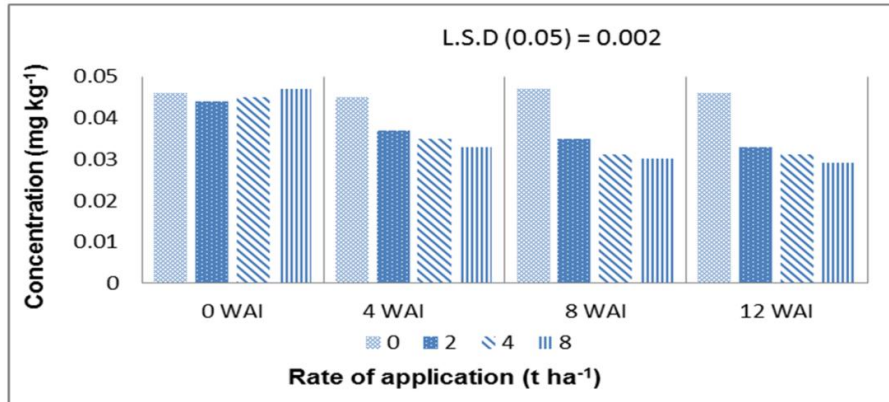


Fig. 8. Effects of corn cob biochar on water soluble lead of capped tailings

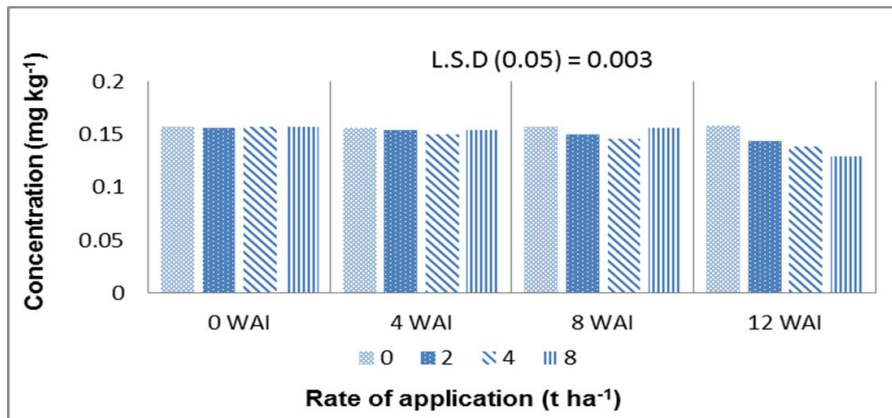


Fig. 9. Effects of corn cob biochar on water soluble lead of uncapped tailings

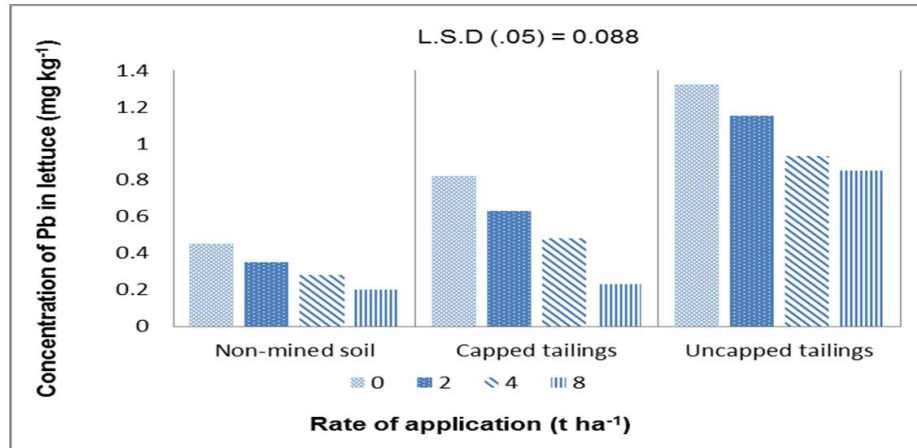


Fig. 10. Bioavailability of lead in *Lactuca sativa* L. after mediation with biochar

The content of lead in lettuce grown on biochar-amended non-mined soil (0.2–0.37 mg kg⁻¹), capped (0.2–0.6 mg kg⁻¹) and uncapped (0.85–1.15 mg kg⁻¹) tailings were lower than the permissible limits of 2.0–2.5 mg kg⁻¹ [22] and 2.0 mg kg⁻¹ [27] in food items. Lettuce cultivated on non-mined soil, capped and uncapped tailings would therefore have no adverse effects on the health of humans after consumption with respect to Pb toxicity. However, with the more stringent maximum limit of 0.3 mg Pb kg⁻¹ dry matter set by [28] only capped tailings and non-mined soil mediated with 8 t ha⁻¹ and 4 t ha⁻¹ biochar, respectively would be safe for human consumption. It is important to stress that lead is bio accumulative in the human body. This implies that even if the level of Pb in the lettuce is below permissible limit, continuous consumption of such vegetable may eventually reach the allowable limit hence causing adverse effect on human health. Lettuce with Pb content of 0.85 mg kg⁻¹ harvested from 8 t ha⁻¹ biochar-amended uncapped tailings would not be suitable for human consumption under [28] standards.

4. CONCLUSION

Generally, the application of 8 t ha⁻¹ biochar to soil/tailings resulted in the highest alkalization and lowest concentrations of water soluble and EDTA-extractable Pb of non-mined soil, capped and uncapped tailings. The application of 8 t ha⁻¹ biochar resulted in the highest significant increase alkalinity of non-mined soil and uncapped tailings in contrast to un-amended samples. However, the alkalinity of capped tailings was insignificantly different with the

application of either 4 t ha⁻¹ or 8 t ha⁻¹, although the alkalinity at each rate of application was significantly greater than that of un-amended samples. The increased alkalinity possibly contributed immensely to the reduced concentration of EDTA-extractable and water soluble lead and the immobilization of lead in soil/tailings. The retention of adsorbed Pb, as evidenced by the reduced concentration of EDTA-extractable and water soluble Pb in soil/tailings, resulted in significantly lower content of lead in the lettuce grown on biochar-amended soil/tailings compared to un-amended samples.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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