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Biochar Produced at Different Temperatures as Bioamendment to Reduce Bioavailability of Heavy Metals

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Abstract: Biochar (BC) is considered as a promising material that can be used as a cost-effective soil amendment to immobilize the heavy metals in contaminated sites. Soil where shooting practices are conducted is extremely contaminated with heavy metals, exclusively by Pb and Cu, owing to the bullets and bullet fragments. In this study, woody BC, prepared by slow pyrolysis of *Gliricidia sepium* biomass at 300 and 500°C with a holding time of 3h and a waste byproduct of the same biomass from a bioenergy industry (BC700) were checked as potential bioamendments for heavy metal immobilization in shooting site soils in Sri Lanka. A pot experiment was carried out by adding BC together with soil at three different percentages i.e.1.0, 2.5 and 5% (w/w). Soil without amendments served as the controls. All treatments were done in triplicate and arranged in a completely randomized design (CRD). Following 6th week, the sequential extraction method was conducted to determine the bioavailability of Pb and Cu. The initial soil pH was 5.64 and a relatively low electrical conductivity value was observed (28.41µS/cm). The total contamination levels of Pb and Cu in the soil were 20800 and 1860 mg/kg and the exchangeable concentrations are 16314.53 and 913.47 mg/kg, respectively. The pH values of all the treatments lay between 5.64-7.09. Although there was not any significant difference between the treatments, pH showed a slight increase with the application of BC from the higher pyrolysis temperature and with increasing application rate. The highest extractable concentrations of Pb and Cu were observed in the control soil, whereas the highest immobilization of metal percentage was recorded in the 5% BC700 treatment for Pb and Cu, 48.80 and 83.96% respectively compared to control. The results suggested that the addition of BC, which is a waste byproduct of the bioenergy industry at the rate of 5%, has the capability of immobilizing heavy metals from the contaminated soil.

Key words: Bioamendment · Bioenergy · Pyrolysis · Immobilization

INTRODUCTION

Soil contamination with heavy metals particularly Pb and Cu are commonly found and released from several industries and different practices such as waste disposal to landfills, shooting practices, mine tailings, pesticides, sewage sludge, land application of fertilizers, coal combustion and vehicle smoke. The presence of such heavy metals in exceptional concentrations may cause risks and hazards to humans and the ecosystem through direct ingestion or contact with contaminated soil, food chains, drinking of contaminated groundwater, reduction in food safety and marketability *via* phytotoxicity and reduction in land usability for agricultural production causing food insecurity [1, 2].

Due to above facts, remediation of such metal contaminated soils is very important. So in recent times, application of biochar (BC) has been renowned as an effective, non-instructive, inexpensive, aesthetically pleasing and socially accepted bioremediation technique to remediate heavy metal contaminated soils [3]. BC is the carbon rich product, which can produce from any waste biomass like, crop residues, manures, forestry residues and from green wastes by thermal decomposition of organic material under limited/no supply of oxygen [4].

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It is considered as latest promising innovation at the movement worldwide due to its universal applications in metal remediation, carbon sequestration and many other functions as a soil amendment[5]. BC addition has not decreased of the total heavy metal content of the soil; however, may reduce the bioavailability and the mobility of metal ions [6].

This study was focused based on woody BC that produced at three different temperatures of 300, 500 & 700°C from biomass of *Gliricidia sepium.* According to the previous evidence, it was hypothesized that the combination of the woody BC is able to alter the immobilization and reduce the bioavailability of Cu and Pb in contaminated soils in Sri Lanka. Thereby, it could reduce the concentration of metals in contaminated site. Therefore the objectives of the study were proposed as,

To assess the potential of woody BC that produced at three different temperatures of 300, 500 & 700°C as soil amendment to immobilize the bioavailability of Pb and Cu in contaminated soil.

To compare the effectiveness of BCs at different application rates, 1, 2.5 and 5% on immobilization of heavy metals.

MATERIALS AND METHODS

Soil Sample Collection: The pre-characterized bulk surface sample of contaminated soil was used and it was collected from Diyadhalawa, Sri Lanka. These soil samples are contaminated with heavy metals such as Pb and Cu due to shooting practices. The collected soil samples were mixed and standardized into one sample, air dried and sieved mechanically to particle size of < 2 mm of prior to experiments [4].

Preparation of BC: Three types of BC which produced from wood chips of *Gliricidia sepium* were used in this study and those were obtained at different temperatures of 300(BC300), 500(BC500) and 700°C(BC700). Dried *Gliricidia sepium* wood chips were used as the biomass to produce BC. *Gliricidia sepium* wood chips were oven dried at 60 °C for 24 h [7]crushed and ground to <1.0 mm size particles. The obtained biomass was pyrolysed at three different temperatures of 300, 500 and 700°C in a muffle furnace under a limited supply of air. For the complete carbonization of biomass, a holding time of 3 h was applied for each peak temperature [8]. The BCs produced at 300, 500 and 700 °C were allowed to cool inside the furnace overnight and taken as BC300, BC500 and BC700, respectively.

pH and Electrical Conductivity (EC) of BC: pH and EC of BCs were measured in 1:20 suspensions of biochar-to-water using a digital pH meter (702SM Titrino, Metrohm, Swiss) and EC meter (Orion 5 star meter, Thermo Scientific), respectively after shaking in a horizontal shaker at 100 rpm constant shaking rate for 4 h.

Experimental Setup: The air dried and 2 mm sieved contaminated soil samples were used in pot experiment to assess the potentiality of BC as soil amendment to immobilize the bioavailable toxic metals in contaminated site. Untreated soil was used as control. Pot mixture was prepared by mixing 250 g of soil with three BCs (BC300, BC500 and BC700) separately according to the mass fraction of 1.0, 2.5 and 5.0 % (w/w). After filling of potting mixture, these filled pots were placed in a controlled dark room and the mixtures were allowed to achieve equilibrium during two weeks of time. After the equilibration period the pots were transferred into a poly tunnel and kept for six weeks.

Soil analysis

pH, EC and Total Organic Carbon (TOC): The pH and EC of the soils were measured using a digital pH meter (702SM Titrino, Metrohm, Swiss) and EC meter (Orion 5 star meter, Thermo Scientific), respectively after shaking in a horizontal shaker at 100 rpm constant shaking rate for 4 h. TOC of the soil was measured by the procedure of Blaker, 1976.

Sequential Extraction Procedure (SEP): The SEP is a selective extraction process to mimic the trace metals in the soil solid fractions and in different geochemical segments [9]. SEP was carried out for soil sample, which was taken out from each pot after six weeks from treatments according to the standard method illustrated by [10]. Here the concentrations of Pb and Cu in the filtered supernatant were measured by using the atomic absorption spectrophotometer (AAS GBC 933A).

Statistical Analysis: The experimental design was set up in a Complete Randomized Design (CRD) with twelve treatments and three replicates. Difference among treatments was tested with analysis of variance (ANOVA) and mean separation were conducted using DNMRT procedure using SAS 9.1 software.

RESULTS AND DISCUSSION

pH and EC of BC: While, the pH of BCs (in 1:20 ratio of BC to water) produced from *Gliricidia sepium* biomass lied in the series of weakly acidic to alkaline, depending on pyrolysis temperature. The lowest pH value 6.8 recorded at lowest pyrolysis temperature 300 °C. However, this value amplified sharply and reached 9.3 at 500°C and 10.4 with temperature of production at 700 °C (Table 1). The increase in pH with rising pyrolysis temperatures is principally due to separating of alkali salts such as Na, K, Ca and Mg from organic matrix and the loss of acidic functional groups in the feed stock at high temperatures [11, 12].

Furthermore, high pH values entail the capability of BCs to immobilize heavy metals and mobilization of oxy-anions in heavy metals contaminated soils [7, 13]. In addition to this, [7] accounted that BC-induced increases in soil pH could also manipulate the sorption of metals. Alteration in pH (Δ pH) values specified that the net surface charge of BC that was produced at low temperature is negative and the surface tents to befall more positive with the increasing pyrolysis temperatures [11].

The EC acts as an indicator for the salinity. The EC values of BCs produced at 300°C, 500 °C and 700°C were 212.4, 537.5 and 1703.5µS/cm correspondingly. These outcomes imply that BCs produced at high pyrolysis temperatures may amplify the soil salinity when they are applied to the soil as amendments.

Soil Properties

Influence of BC amendments in changes of soil pH, EC and TOC: The influence of BC amendments on changes in some soil physiochemical properties of soil such as pH, EC and TOC of contaminated soil are tabulated in Table 2. The pH values of all treatment obtained from the study is laid between 5.64 and 7.09, at the same time none of them were significant at 95% probability level. Though, the pH values in Table 1, has shown a slight increase in pH with rate of BC application and its pyrolysis temperature.

In the presence study, the soil pH is amplified to certain level by the addition of BC. This is due the presence of alkali elements such as Ca, Mg and Na and the existence of OH ions in BC. Yuan [14] also noted similar type of results on the soil pH when they applied the BC as soil amendment during their experiments, for the BC 700 it is around10.10. Basic cations such as Ca, Mg, K and Na in biomass are altered into oxides, hydroxides and carbonates that can stick on with BC during pyrolysis progression [7]. Due to the dissolution of the alkaline substances, which boost the soil pH. Moreover several authors have reported, that the slight increase in pH may be due to decarboxylation of organic anions and ammonification in soil [15, 16].

Table 1: pH and EC of BC

Treatments	EC (µS/cm)	pH (water)
BC300	212.4	6.8
BC500	537.5	9.3
BC700	1703.5	10.4

Table 2: Influence of BC amendments in changes of soil pH, EC and TOC

Treatments	pH	EC (µS/cm)	TOC(mg/kg)
Control	5.64^{j}	28.41^{j}	5.23^{j}
1% BC300	6.23^{i}	32.77^{i}	6.26^{i}
1% BC500	6.39^{h}	38.08^{g}	6.32^{h}
1% BC700	6.59^{f}	39.02^{f}	6.34^{f}
2.5% BC300	6.48^{g}	37.04^{h}	6.33^{g}
2.5% BC500	6.72^{e}	39.21^{e}	6.50^{e}
2.5% BC700	6.85^{c}	42.50^{d}	6.55^{d}
5% BC300	6.76^{d}	51.14^{c}	6.82^{c}
5% BC500	6.88^{b}	63.04^{b}	6.84^{b}
5% BC700	7.09^{a}	70.70^{a}	6.91^{a}

Means with the same letter are not significantly different

After the addition of BC, EC of the soil also increased significantly than the non-amended soil. EC values of the all treatments fall between 28.41 - 70.70 µS/cm. The increasing pattern could be observed together with concentration of BC and its preparation temperature. The treatment level of 5% BC700 showed highest EC value when compared to other treatments. The increase in soil EC in the presence of BC has also been noted in earlier studies [17].

The same pattern of changes was observed in case of soil TOC and it was laid between 5.23 and 6.91 mg/kg. As shown in Table 4.5, the contents of TOC in 5% BC 700 amended polluted soil was nearly 2.0 folds higher than that of the BC unamended soils. In case of TOC, which also increased significantly with the application of BC due to the adding of high carbon into the soil [18]. The pH, EC and TOC of contaminated soil increased significantly with increasing concentration of BC amendment. So increment of BC application rises the quality of soil physiochemical properties [18].

Bioavailability of Heavy Metals: In soils metal are partitioned with different geochemical phases in the soil [9] as in the form of exchangeable and bound with carbonates, Fe-Mn oxides, organic matter and residual fraction [19, 20]. Exchangeable fraction is considered as readily mobile and available to plant [21, 22].

Soils in Diyatalawa area is in critical condition due to the prominent concentrations of toxic heavy metals Pb and Cu due to shooting practices conducted by Sri Lankan forces. The initial concentration of total and bioavailable concentration of Pb and Cu are

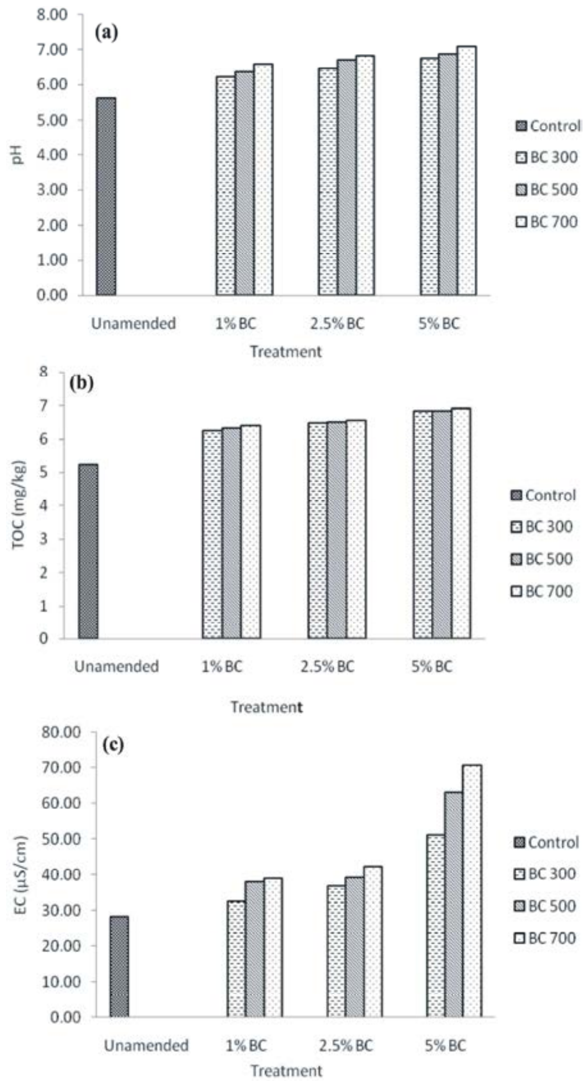

Fig. 1: Effects of BC amendments in changes of soil (a) pH, (b) EC and (c) TOC

20843.28, 1861.9 mg/kg respectively. For the sequential extraction process, soil sample was taken after six weeks from the day of BCapplication. This period was decided for the effectiveness of work, based on the previous studies [23].

The $MgCl_2$ extractable fraction of Pb and Cu significantly decreased with the combination of BC. The reduction of bioavailability of meals increased significantly with BC production temperature and its rate of application (Fig-2). The reduction in the accumulated concentration of exchangeable fraction of heavy metals in contaminated soil samples with different rate of BC application and its pyrolysing temperature is expected due to the immobilization of Cu and Pb.

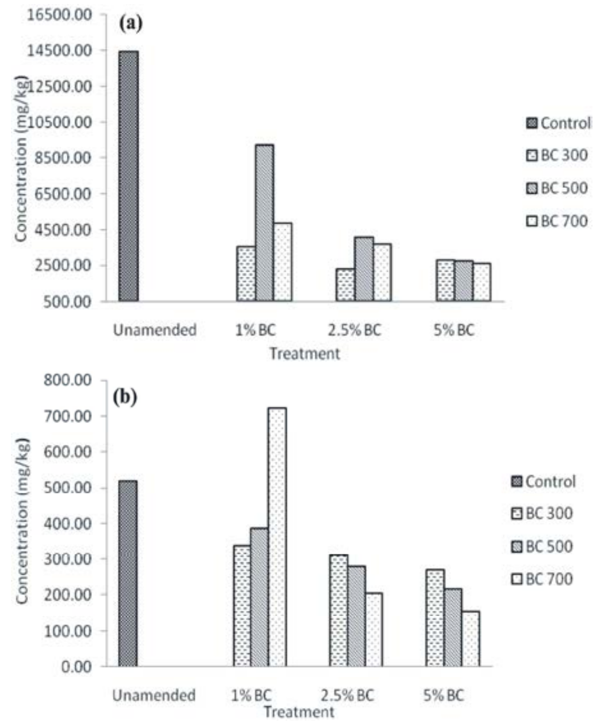

Fig. 2: Availability of metals (a – Pb and b – Cu) with BCs amendedment in heavy metal contaminated soil

The most effective treatment is 5% BC700, because the removal efficiencies of both Pb and Cu were 48.80 and 83.96% correspondingly compare to control. At the same time, with increasing concentrations of BC700 (i.e., 1, 2.5 and 5%), exchangeable concentration of Pb and Cu decreased by 1470.97, 1342.50 & 1104.90 and 44.40, 44.30 & 16.47 mg/kg, respectively.

The BC has the ability to reduce metal solubility by raising of soil pH as alkaline nature and through the retention of cation exchange site [24]. At the same time, the preferable pH to determine the availability of heavy metal is acidic [25]. An increase in soil pH due to BC amendment may lead to decrease the immobilization of heavy metals and ion precipitation.

Because there are many functional groups such as carboxlic, alcohol and hydroxyl groups on the surface of BC, it is easy to form complexes with heavy metals and these groups [26]. BC has the capacity to retain the metals together with application rates and their pyrolysing temperature.

Mesopores are highly available for adsorbing metals due to the lack of many functional groups [19]. Therefore, the reduction heavy metals in the presence of BC may improve the quality of soil from critical condition.

The present study suggested that the application of 5% BC700 enhance the reduction of an accumulated exchangeable metal fraction in the soil.

On the other hand, all the physiochemical properties of BC mainly depend on pyrolysing temperature. According to the study, the obtained results showed a significant decrease in the bioavailable metal concentration with a raise in BC amendment and the application of BC under elevated pyrolysing temperature.

In overall, the results demonstrated that the application of BC at the rate of 5% enhances the quality of soil quality by immobilizing toxic metals significantly. At the same time soil properties such as soil pH, EC and TOC also improved by the application of 5% BC.

CONCLUSION

It can be concluded that BC has been renowned as a best bioremediation technique to enhance the quality of soil, which is severely affected by accumulated heavy metals. Results of the presence study suggest that BC has the potential to significantly affect the behavior of metals in contaminated soil, by altering their solubility and availability.

BC, which was generated from bioenergy industry at 700 °C was the most effective amendment when compare to other BCs, BC300 and BC500. By the application of 5% BC700, the field activities can be carried out to enrich the quality of affected soil in Sri Lanka.

Furthermore, additional studies should be designed to analyze the effect by increasing the application rate of BC above 5%.

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