

Evaluating Heavy Metal Mobility in Contaminated Soils Amended with Biochar: A Kinetic Perspective

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SUMMARY

The extensive contamination of heavy metals (HMs) in Pakistani soils has a severe impact on the health of both the plants and soil. The application of biochar as a soil amendment to immobilize heavy metals is an emerging technique. A lab experiment was carried out at institute of soil science Arid Agriculture University Rawalpindi using wood-derived biochar prepared at two different temperatures (400 °C and 600 °C). Naturally, chromium (Cr) contaminated soil was used in the lab study following 1% and 3% biochar levels (w/w). Heavy metal mobility was characterized by using equilibrium; the kinetic extraction parameter was linked with the labile and slow labile fractions. Results showed that the concentration of Cr increased with an increase in biochar production temperature and rate. The extraction of Cr at equilibrium (24 h) was higher than that of the other kinetic extraction, and the highest Cr content was observed at 24 h in all treatments. While in labile fraction and a slowly liable fraction the extraction of the slowly labile fraction (Q2) is higher than a labile fraction (Q1) and the extraction time for a labile fraction (k1) was less and for slowly labile fraction extraction time was higher in all the treatments, while the lowest value of was R2 0.9485 and SEE 0.9485. Trace metal localization and availability of chromium content increase with decreasing physical size fraction, higher content was recorded in finer fractions 0-50 µm, and low content was recorded in course texture fractions 300-2000 µm in with and without biochar amended soil. Trace metal localization and availability increased with the increment of biochar rates and biochar temperature.

Keywords: Kinetic, Equilibrium, Biochar, Labile, Heavy metal, Chromium

INTRODUCTION

The prevalence of heavy metals in soil, water, and air is a global issue that poses an increasing hazard to the ecosystem. Soils, water, and air are all potential sources of heavy metal pollution in the environment. Heavy metal pollution in soil is a severe concern brought on by human activities, including mining (Kumar et al., 2017), industry (J. Liu et al., 2018), agricultural practices (Abdelhafez et al., 2012), or treated wood buildings (Abdelhafez et al., 2009). According to Abdelhafez et al. (2012) and Behbahaninia and Mirbagheri (2008), excessive presence of heavy metal

in farmlands contaminates the agricultural produce and alters its quality which poses serious threats to final consumers. Currently, various techniques are present for the treatment of heavy metal contaminated soils, however these are not feasible due to the complex methodologies and higher operating cost (L. Liu et al., 2018).

These techniques include excavation, thermal treatments, electro kinetic, chemical precipitation, and leaching. When biomass is pyrolyzed at a low temperature (700 °C), it produces biochar, a kind of charcoal (DeLuca et al., 2009). Depending on the moisture level of the feedstock, the production of biochar typically produces more energy than it consumes. The physicochemical parameters of Biochar (such as composition, particle and pore size distribution) that define its acceptability for a specific application as well as dictating its behavior, transport, and destiny in the environment are primarily controlled by pyrolysis settings and feedstock characteristics. Heavy metals are characterized as chemical elements possessing a density exceeding 5 g cm⁻³ or a specific gravity exceeding fivefold that of water. (Njoga et al., 2021). These metals are universal and determined pollutants exist in a myriad of industrial wastes. For instance, copper, mercury, lead, zinc and cadmium are considered as heavy metals and causes environmental hazards. Some heavy metals at high concentration are harmful to all types of life include human being, animals, plants and other microorganisms. Heavy metals contamination is a serious global problem as these metals remain persistence and non-biodegradable in soil. In spite of mechanical progressions, removal of metal from soil is neither effective nor simple (Dickinson 2000).

Major concern regarding heavy metals contamination in agricultural soils is that these metals enter in food chain through plants uptake. Although their availability depends on soil type, physical and chemical conditions (Basta et al., 2005). Therefore, sustainable usage of contaminated agricultural soil requires specific management to minimize the risk of trace metals. Sialkot, one of the major cities in Pakistan, has a unique combination of agricultural farms and industries. However, the proximity of industrial facilities to agricultural lands results in the direct disposal of sludges and waste into waterways (Qadir et al., 2008). As a consequence, farmers often resort to using this contaminated water for irrigation purposes, leading to crops that may contain traces of heavy metals. This situation poses a severe threat to the health and well-being of consumers. Biochar is the solid product from the pyrolysis of waste biomass, such as agricultural and forestry residues, manures and dead animals (Yang et al., 2016b). Recently Biochar is used as soil amendment to remediate heavy metals in contaminated soils. It increases heavy metal immobilization and hence decreases the bioavailability of metals in contaminated soils (Verheijen et al., 2010). In addition, biochar has been effectively used for the remediation of naturally or anthropogenically heavy metal contaminated agricultural soils. According to Park et al. (2011), the application of biochar was effective in reducing phytotoxicity, immobilization and bioavailability of heavy metals in soil. Furthermore, it has high capacity to stabilize heavy metal in soil, and improve quality of the polluted soil by reducing heavy metals uptake by plant. Besides, Biochar is a good sorbate of organic and inorganic pollutant, because of its structure and larger surface area.

Cao et al. (2016) found that FYM-biochar produced at ≤500°C removed Pb and atrazine by 100% and 70%, respectively from aqueous solution. Mechanisms to

immobilize the heavy metal through adsorption on to biochar are surface-precipitation, electrostatic interaction, and chemisorption, etc. (Lu et al., 2012). Numerous studies have investigated the application of biochar as an amendment to remediate soil contaminated with heavy metals. However, a noteworthy research gap exists when it comes to comparing the effectiveness of biochar produced at low and high pyrolysis temperatures. Furthermore, the understanding of how distinct soil particle fractions influence the release and availability of chromium (Cr) in biochar-amended contaminated soil remains considerably limited. Hence, the present study was conducted to address these objectives, focusing on heavy metal mobility and availability in biochar-amended contaminated soil.

Materials and Methods

Biochar preparation and characteristics

Biochar was prepared from solid raw material through pyrolysis process. In this study, the biochar was produced from acacia wood (*Leucocephala glauca* Benth) in the laboratory. The *Acacia* wood was collected from the University research farm and broken down into small pieces followed by drying it in an oven. Dry small pieces of acacia wood were placed in the Muffle furnace at 400 and 600°C pyrolysis temperature for 1 to 2 h. Both biochar (BC₄₀₀ and BC₆₀₀) were ground and passed through a 2 mm sieve and then stored in resealable plastic bags for further analyses such as pH, EC, and Cr concentration.

Soil collection and analysis

Naturally Cr contaminated soil was collected at 0-20 cm depth from the Sialkot region, it was air-dried, and then passed through a 2-mm sieve. A part of the soil was subjected to analysis to determine its pH, organic matter (OM) content, electrical conductivity (EC), and chromium (Cr) levels. The remaining portion of the soil was set aside for the incubation study. The pH and EC were measured from soil (10 g) and distilled water (20 mL) suspension (1: 2 ratio) by using standardized pH meter and electrical conductivity meter, respectively (McLean, 1983). The total Cr content was analyzed by digesting 1 g soil with 2:1 digestion mixture (nitric acid and per chloric acid) in digestion tubes and heated them at 350°C until white fume are clear and then cooled at room temperature, filtered and made its volume up to 50 ml with distilled water and then Cr content was measured by atomic absorption spectrophotometer (AASPM).

Lab incubation experiment

The lab experiment was conducted by mixing the BC₄₀₀ and BC₆₀₀ biochar in naturally Cr contaminated soil at 1% and 3% (w/w), respectively. These mixtures were subsequently incubated at room temperature for one month while maintaining a soil moisture level at 50% of its water holding capacity. To ensure randomization and statistical validity, all treatments, including the control without any biochar, were arranged using a Completely Randomized Design (CRD) with three replications.

Kinetic assessment of metal through chemical extraction

Kinetic extraction was performed at different short and long time intervals till

equilibrium (24 h) is achieved. Different assays were performed to get optimal extraction condition, especially Ethylene diamine tetra acetic acid (EDTA) concentration, pH of extracted and mass-to-volume ratio. The soil samples were first sieved through 2mm sieves and then transferred to a beaker. Subsequently, the soil was shaken with an EDTA solution at 300 rpm on a mechanical shaker for different periods of time. Following the shaking process, the suspension was immediately subjected to centrifugation for 10 minutes. The resulting supernatants were filtered through filter paper and stored at 4°C for subsequent measurement of the heavy metal content. To analyze the data obtained from the kinetic extraction, we utilized the "two first-order reaction model", which was previously reported by Labanowski et al., 2008. This model enabled us to accurately quantify the two metal fractions.

$$Q = Q_1 (1 - \exp^{-k_1 t}) + Q_2 (1 - \exp^{-k_2 t})$$

Where Q_1 = liable metal fraction, Q_2 = slowly labile fraction. $1/K_1$ are the release time of labile values and $1/K_2$ is release time of slowly metal pools were calculated from extraction rate.

Physical size fractionation of trace metal

For the physical fractionation of soil, followed the method outlined by Fernandez et al., 2010. Initially, the soil was air-dried and then passed through a 2mm sieve. Once sieved, a 50g soil sample was dispersed in 125ml of deionized (DI) water, and the suspension was shaken for 16 hours using a rotating shaker. After shaking, wet sieving was conducted using stainless steel sieves with mesh sizes of 50µm, 200µm, and 300µm. This allowed for the separation of the soil into four fractions: 2000-300µm, 300-200µm, 200-50µm, and <50µm. The fractions sized 2000-300µm, 300-200µm, and 200-50µm were collected through sample sieving, while the <50µm fraction was obtained by centrifuging the soil suspension at 3000rpm. The <50µm fraction was then stored in polyethylene containers after freezing, while the remaining fractions were dried at 60°C and also stored in polyethylene containers. The heavy metal content of each fraction was measured.

Statistical analysis

Statistical analysis was conducted using XLSTAT version 2010 software. An ANOVA and Pearson correlation test were carried out to examine the relationships between the parameters describing both chemically and physically fractionated metals. To model the kinetic extraction data, Sigma Plot 9.0 software (SPSS Inc.) was employed. The validity of the modeling was assessed using statistical parameters such as the coefficient of fitting (R^2) and the standard error of estimate (SEE).

RESULTS AND DISCUSSION

Characteristics of Biochar

The biochar was produced from acacia wood (*Leucocephala glauca* Benth) at different temperatures (BC₄₀₀ and BC₆₀₀) and analyzed for pH, EC, and Cr content. Results has shown that the pH of BC₄₀₀ was observed (7.5), and BC₆₀₀ was (8.1), while, the EC of biochar was 1.52 and 1.22 d S m⁻¹ for BC₆₀₀ and BC₄₀₀, respectively. The Cr contents of biochar BC₄₀₀ and BC₆₀₀ were 1.85mgkg⁻¹ and 2.0mgkg⁻¹ respectively. Biochar chemical and physical properties largely depended on the

burning temperatures and time duration. The charring temperature was consistent with that reported by Zimmerman (2010). Apart from temperature and time intervals (Demirbas 2004) reported that the yield depends on heating rates, particle size, and quality of the organic material.

Soil pre and post heavy metal treated characteristics

The pH of the soil sample was observed (7.6) while, the EC of soil was 1.1 d Sm^{-1} , respectively. The soil has low organic matter (0.45%), and the texture of soil was observed as loam. The total Cr contents were 3900 mg kg^{-1} . After one month of biochar amendment to Cr contaminated soil, significant differences were found in Cr concentration. Table.1 demonstrates high difference in availability of the Cr control (3900 mg kg^{-1}) and biochar amended soil 1%BC₄₀₀ (3923 mg kg^{-1}), 3%BC₄₀₀ (3940 mg kg^{-1}), 1%BC₆₀₀ (3940 mg kg^{-1}), 3%BC₆₀₀ (3950 mg.kg^{-1}). Results showed that pH, EC, and organic matter concentration of contaminated soil increase with biochar application. A similar result reported by (Balwant et al., 2018). Cr concentration in soil follow the order Control > 1%BC₄₀₀ > 3% BC₄₀₀ > 1%BC₆₀₀ > 3% BC₆₀₀, revealing biochar application has decreased the concentration of Cr in soil. The majority of biochar exhibits alkaline properties, thereby capable of increasing the soil's pH level and reducing the mobility of heavy metals within the soil matrix. (Ali et al., 2017). Alkaline pH of biochar and high CEC affected basic soil properties significantly in cases of sandy soil, while in loamy soil with higher pH and better sorption properties the effect was less significant. Observed increases of soil pH after biochar application to sandy soil. The alkaline pH of biochar, coupled with its high Cation Exchange Capacity (CEC), had a substantial impact on basic soil characteristics in sandy soil. In contrast, its influence was relatively less pronounced in loamy soil, which inherently possesses a higher pH and higher sorption properties. Notably, biochar application led to noticeable elevations in soil pH when applied to sandy soil. (Medyńska-Juraszek and Ćwieląg-Piasecka, 2020)

Extractable Cr at equilibrium

Results in Table. 2 showed the concentration of EDTA extractable Cr in biochar amended and untreated naturally Cr contaminated soil labeled the treatments as 1%BC₄₀₀, 3% BC₄₀₀ 1% BC₆₀₀, and 3% BC₆₀₀ soil sample at equilibrium. The result showed that the extraction of Cr was significantly different from each of all treatments at equilibrium (24 h). The extraction of Cr was done at different time intervals starting from 15min to 24 h, whereas at 24 h, the maximum extraction was recorded. The result recorded has shown that the concentration of Cr follows the order 3%BC₆₀₀ > 1%BC₆₀₀ > 3%BC₄₀₀ > 1%BC₄₀₀ > Control. The increasing time intervals with EDTA extractor the extraction of Cr increased. Chromium extractable content was observed significantly differ in all treatments. This result may suggest that the chromium is the major soil contaminant in soil. The efficiencies of extraction for chromium is lower in control, 1%BC₄₀₀, than in 3%BC₄₀₀, 1%BC₆₀₀ and high in 3%BC₆₀₀ soil biochar soil samples. The result also showed that the concentration of Cr increase with an increase in biochar production temperature and rates of biochar (w/w) to naturally Cr contaminated soil. The extraction of Cr increase with EDTA with increasing of time interval the more extraction was recorded at equilibrium for

all treatments. Extraction of Cr at equilibrium for control ($1891.66 \text{ mg kg}^{-1}$), 1%BC₄₀₀ ($2328.33 \text{ mg kg}^{-1}$), 3%BC₄₀₀ ($2463.33 \text{ mg kg}^{-1}$), 1% BC₆₀₀ ($2505.66 \text{ mg kg}^{-1}$), and 3% BC₆₀₀ ($2828.33 \text{ mg kg}^{-1}$).

These findings are comparable to (Kartal et al., 2002) that the Cr was removed with extraction time and the EDTA concentration. Letters present significant difference between with and without biochar amended naturally Cr contaminated samples. The availability of Cr increased due to biochar addition, the highest availability was observed at 3%BC₆₀₀ which is higher than all of the other treatments, which are in line of findings by (Ahmad et al., 2022) who recorded highest Cr availability at highest biochar rates 10%, and stated that the bioavailability of Cr increase by an increment of soil pH due to biochar (alkaline resource). Santos et al. (2010) have initiated a lower percentage of EDTA metal extractions at balance for silty textured soil polluted through mineral fertilization. It was concluded that chromium concentration follows the order as pyrolysis temperature and the amendment of biochar at different ratios to contaminated soil extracted more than 80% of the organic soil Cr content, and may propose that chromium is the significant chromium contamination in the soil. Furthermore, the results also indicated that the amount of chromium increased with the increment of biochar producing temperature and percentage of biochar (w/w). In the above results, the maximum extraction was ($2828.33 \text{ mg kg}^{-1}$), which were observed in 3%BC₆₀₀ treatment, and the minimum extraction ($2328.33 \text{ mg kg}^{-1}$) at equilibrium was observed in 1%BC₄₀₀ at low pyrolysis temperature and the low ratio of biochar.

Kinetically-defined labile and slowly labile Cr fraction

Table 2. presents the slow labile fraction (Q_2) and labile fraction (Q_1) metal fraction for chromium of all samples of soil treatments, release time of these fractions (k_1 and k_2) and the model validation parameters, (0.9485) was the lowest value of R^2 and (29.95) was the lowest data SEE in the modeled data confirming good fit of data molding. EDTA is used for the extraction of heavy metal from naturally Cr contaminated soil. The labile (Q_1) is defined as the fast extraction of cations, and slowly extracted cations are called as slow labile (Q_2). Results showed the ratio between the slowly labile and labile pools and predicted that the slow labile pools are high than labile pools. The labile fraction of Cr is lower than the slow labile fraction in all treatments; such a result had been already recorded for Zn, Pb, Cu, and Cd by Santos et al. (2010), while Labanowaski et al. (2008) were recorded higher value of labile metal fraction than slowly labile fraction. In the present study, the soil had similar texture but the temperatures, and rates of biochar pyrolysis were different. The biochar was applied on (w/w) to naturally Cr-contaminated soil. The relationship between labile fractions and slow labile fractions revealed a significant difference among control, 1%BC₄₀₀, 3%BC₄₀₀, and 1% BC₆₀₀, and 3% BC₆₀₀. Kinetic extraction results generated information about the extraction of Cr at equilibrium and more detail about the availability of Cr. The availability of Cr decreases in biochar amended soil samples at equilibrium, which described the decrease in the labile pool (Q_1) and increase in the slowly labile pool (Q_2). For both labile and slow labile fraction the releasing time was lower for treatment of control, 1%BC₆₀₀ and 3%BC₆₀₀ than 1%BC₄₀₀ and 3%BC₄₀₀. while the value of k_1 was around 4-15 min and k_2

values was about 196-1000 min were are in the same result was published by Labanowski et al. (2008). While the result published for trace metal is around 3min for k_1 and about 110-550 were for k_2 has already noted by Varrault & Bermond (2011). Upon comparison labile and slow labile result showed significant difference in all treatments, control (799.4mgkg^{-1}), (1095.2mgkg^{-1}), 1%BC₄₀₀ (1095.2mgkg^{-1}), (1337.5mgkg^{-1}), 3%BC₄₀₀ (1322.3mgkg^{-1}), (1478.0mgkg^{-1}), 1%BC₆₀₀ (952.1mgkg^{-1}), (1509.9mgkg^{-1}) and 3%BC₆₀₀ (1086.3mgkg^{-1}), (1757.9mgkg^{-1}). The result showed that the extraction time for labile and slow labile fraction, k_1 releasing time for labile pools in the lowest time in minutes was as recorded for 1%BC₆₀₀ (4.81min), 3%BC₆₀₀ (4.65min), and control (8.46min) and highest time was recorded for 1%BC₄₀₀ (13.75min) and 3%BC₄₀₀ (15.22min), while k_2 was the releasing time for slowly pools lowest time was recorded in 1%BC₆₀₀ (178.57min), 3%BC₆₀₀ (196.07min), and control (294.1min) and the highest releasing time was noted in 1%BC₄₀₀ (588.23min) and 3%BC₄₀₀ (1000min). For both labile and slow labile fraction the releasing time was lower for control, 1%BC₆₀₀, and 3%BC₆₀₀ than 1%BC₄₀₀ and 3%BC₄₀₀. The results of this study indicated that slow labile fraction (Q_2) and (Q_1) metal fraction for chromium of all experimented samples of soil, release time of these fractions (k_1 and k_2), and the lowest value of R^2 was (0.9485) while the lowest data (0.9485) was observed in the modeled data SEE. Results also indicated that the relation between the labile and slow labile pools, in which the slow labile pools are high than labile pools (ratios always >1). Moreover, in the present study, the soil has similar textured but different biochar pyrolysis temperatures and ratios (w/w).

Cr localization in the physical size fraction

Figure. 1, 2 showed that the distribution of size fraction according to soil texture. The result showed that the Cr concentration higher in finer fraction 0-50 μm in all treatments and lowered in 300-2000 μm . (Iqbal et al., 2013) investigated that the metal availability increase with the decreasing of fraction size, the finer fraction has more metal concentration then coarse fraction. The Cr content increase with the decreasing of the physical size of fraction in all treatments where the highest was recorded in 0-50 μm . Comparison of Cr distribution between with and without biochar amended soil shown similar Cr content was observed in coarser fraction but higher Cr content in finer fraction (0-50 μm). This unimodal distribution with metal preferentially located in finer fraction (0-50 μm) has already been reported for non-polluted soil and polluted soil (Fernandez et al., 2010) and consistent high reactivity of this fraction. The result showed that 300-2000 μm control less significantly different with biochar (3.7872) produced at BC400 and applied at 1% (5.4086), 3% (6.0070) and highly significant than biochar produced at BC600 and applied at 1% (6.1621), 3% (6.1681). Physical size fraction of 200-300 μm , the control (9.2017) and 1%BC400 (9.0163) has no significant difference but less significantly differs from 3%BC400 (10.644) and highly significantly differs than 1%BC600 (11.469) and 3%BC600 (11.811), and also similar for the physical size fraction of 200-300 μm . Moreover, for physical fraction <50 μm , the control (73.855) has no significant difference with 1%BC400 (72.447) and less significantly different than 3%BC400 (69.013) and highly significantly different than 1%BC600 (67.000) and 3%BC600 (66.190). The result also showed that control has significantly different than 0-50 μm

in all treatments. Upon comparing the Cr availability between control and biochar amended contaminated soil, the Cr content in 0-50 μm fraction was higher than other soil fractions. After one month of biochar application to Cr contaminated soil showed changes in both metal availability and localization. (Alaboudi et al., 2019) reported that the availability of the different forms of Cr in the soil significantly increase with the addition of biochar to contaminated soil. Addition of high rates of biochar to the Cr contaminated soil, the releasing of Cr was more affective and also noted that the mobility of Cr increase with high temperature produced biochar. The Cr percentage was increased with the decreasing of soil fraction size and increasing with high biochar rates and biochar forming temperature. (Alaboudi et al., 2019) investigated that the addition of biochar facilitates the Cr solubility over the change in chemical form from Cr (III) into Cr (IV).

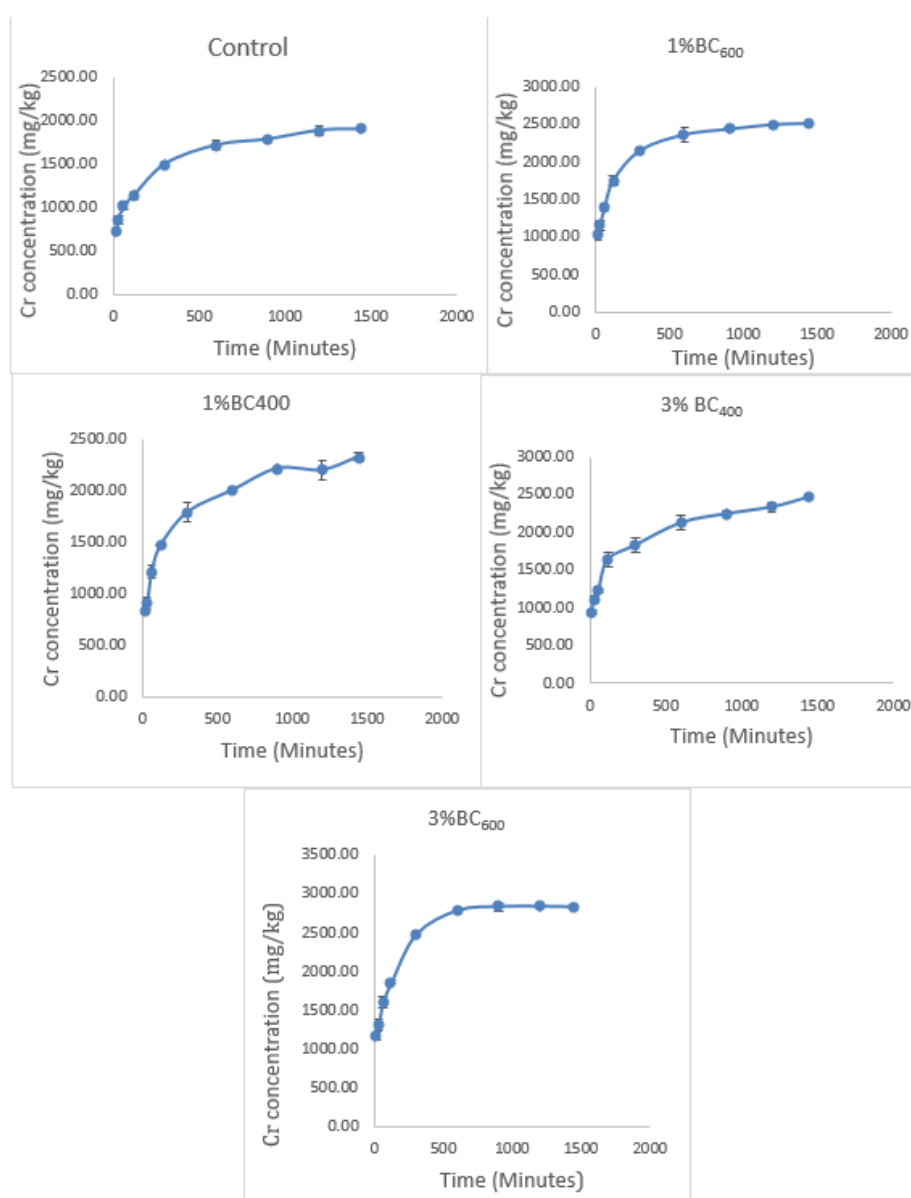


Figure 1: Kinetic extraction of Cr at different time intervals.

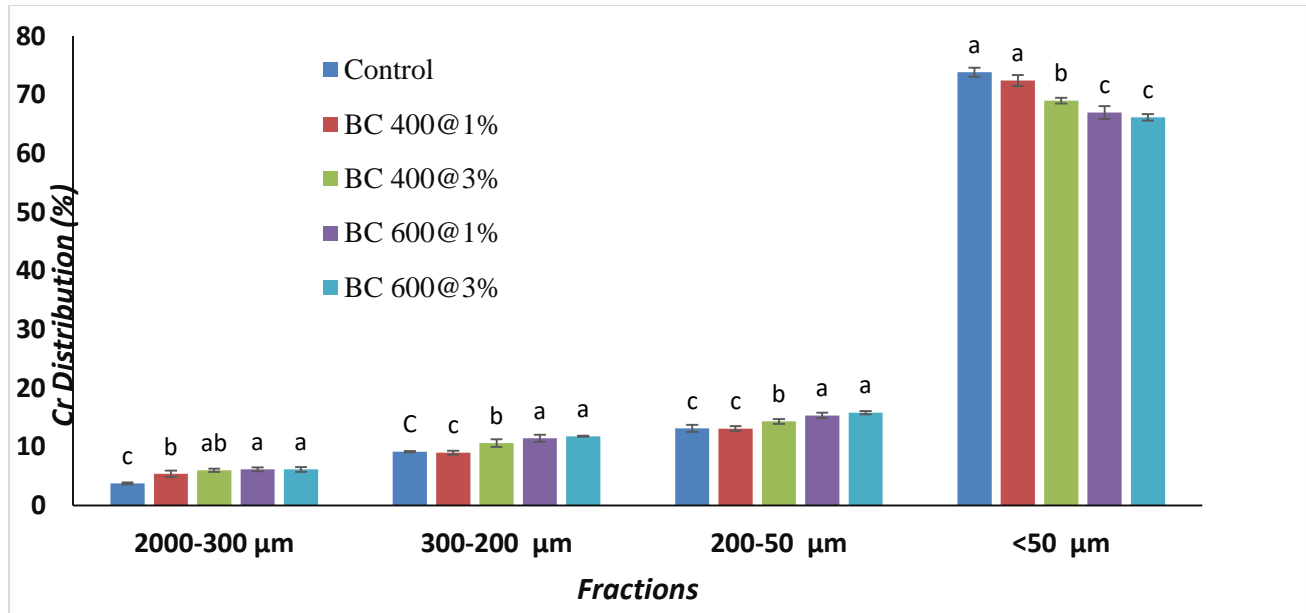


Figure 2. Distribution of chromium in physical size fractionation in with and without biochar amended Cr contaminated soil sample. Among three replicate error bars represent standard deviation. Different letters present significant difference (tukey's test $p < 0.05$ between with and without biochar amended Cr contaminated soil samples.

Conclusions: The concentration of Cr increased with an increase in biochar production temperature and rate. The extraction of Cr at equilibrium (24h) was higher than of the other kinetic extraction, and the highest Cr content was observed at 24 h in all treatments. In labile fraction and a slowly labile fraction, the extraction of the slowly labile fraction (Q2) is higher than a slowly labile fraction (Q1) and the extraction time for a labile fraction (K_1) was less and for slowly labile fraction extraction time was higher in all the treatments, while the lowest value of was R2 0.9485 and SEE 0.9485. Trace metal localization and availability of chromium content increase with decreasing physical size fraction, and low content was recorded in course texture fraction 300-2000 µm in with and without biochar amended soil. Thus it is concluded that trace metal localization and availability increased by the increment of biochar rates and biochar temperature.

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Author's contribution

Janas khan, Imdad Ullah and Qaiser hussain designed the study. Janas khan, Shah zeb Khan and Hasham Ahmad collected field data. Janas khan, Saima Khan, and Akber Ali interpreted results and wrote up the Research article. Maira Zafar and Javaid Hassan revised the draft. All of the authors read and approved the manuscript.

Conflict of Interest: there is no any conflict of interest declared by the authors.

References

- Ali, A., Guo, D., Mahar, A. et al. (2017). Phytoextraction of toxic trace elements by *Sorghum bicolor* inoculated with *Streptomyces pactum* (Act12) in contaminated soils. *Ecotoxicology and Environmental Safety*, 139(5), 202–209. <https://doi.org/10.1016/j.ecoenv.2017.01.036>
- Abdelhafez, A.A., Abbas, H.H., Abd-El-Aal, R.S., Kandil, N.F., Li, J., Mahmoud, W., 2012. Environmental and health impacts of successive mineral fertilization in Egypt. *Clean* 40, 356–363.
- Abdelhafez, A.A., Awad, Kim, Ham, M.S., 2009. K.J., Lim, K.J., Joo, J.H., Yang, J.E., Ok Y.S. Environmental monitoring of heavy metals and arsenic in soils adjacent to CCA treated wood structures in Gangwon Province, South Korea. *Korean J. Environ. Agric.* 28, 340–346.
- Basta, N. T., Ryan, Basta, N. T., Ryan, J. A., & Chaney, R. L. (2005). Trace element chemistry in residual treated soil: Key concepts and metal bioavailability. *Journal of environmental quality*, 34(1), 49–63.
- Behbahaninia, A., & Mirbagheri, S. A. (2008). Investigation of heavy metals uptake by vegetable crops from metal-contaminated soil. *International Journal of Agricultural and Biosystems Engineering*, 2(7), 129–131.
- Cao, X., & Harris, W. (2010). Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. *Bioresource technology*, 101(14), 5222–5228.
- DeLuca, T.H., MacKenzie, M.D., Gundale, M.J., 2009. Biochar effects on soil nutrient transformations. In: Lehmann, J., Joseph, S. (Eds.), *Biochar for Environmental Management: Science and Technology*. Earthscan, London, pp. 251–270.
- Demirbas, A. (2004). Combustion characteristics of different biomass fuels. *Progress in energy and combustion science*, 30(2), 219–230.
- Dickinson, N.M., 2000. Strategies for sustainable woodland on contaminated soils. *Chemosphere* 41, 259–263.
- Fernandez, C., Labanowski, J., Jongmans, T., Bermond, A., Cambier, P., Lamy, I., Van Oort, F., 2010. Fate of airborne metal pollution in soils as related to agricultural management: 2. assessing the role of biological activity in micro-scale Zn and Pb distributions in A, B and C horizons. *Eur. J. Soil Sci.* 61, 514–524.
- Iqbal, M., Bermond, A., & Lamy, I. (2013). Impact of miscanthus cultivation on trace metal availability in contaminated agricultural soils: complementary insights from kinetic extraction and physical fractionation. *Chemosphere*, 91(3), 287–294.
- Kapoor, R. T., Mfarrej, M. F. B., Alam, P., Rinklebe, J., & Ahmad, P. (2022). Accumulation of chromium in plants and its repercussion in animals and humans. *Environmental Pollution*, 301, 119044.
- Kartal, S. N. (2003). Removal of copper, chromium, and arsenic from CCA-C treated wood by EDTA extraction. *Waste Management*, 23(6), 537–546.
- Kumar, A., Maiti, S.K., Tripti, Prasad, M.N.V., Singh, R.S. 2017. Grasses and legumes facilitate phytoremediation of metalliferous soils in the vicinity of an abandoned chromite–asbestos mine. *J. Soils Sediments* 17, 1358–1368.
- Labanowski, J., Monna, F., Bermond, A., Cambier, P., Fernandez, C., Lamy, I., & Van Oort, F. (2008). Kinetic extractions to assess mobilization of Zn, Pb, Cu, and Cd in a metal-contaminated soil: EDTA vs. citrate. *Environmental Pollution*, 152(3), 693–701.
- Liu, J., Liu, Y.J., Liu, Y., Liu, Z., Zhang, A.N., 2018. Quantitative contributions of the major sources of heavy metals in soils to ecosystem and human health risks: a case study of Yulin, China. *Ecotoxicol. Environ. Saf.* 164, 261–269.
- Liu, L., Li, W., Song, W., Guo, M., 2018. Remediation technologies for heavy metal contaminated soils: principals and applicability. *Sci. Total Environ.* 633, 206–219.
- Malik, R. N., Jadoon, W. A., & Husain, S. Z. (2010). Metal contamination of surface soils of industrial city Sialkot, Pakistan: a multivariate and GIS approach. *Environmental geochemistry and health*, 32, 179–191.
- McLean, E. 1983. Soil pH and lime requirement. *Methods of soil analysis: Part 2 Chemical and microbiological properties*. 9: 199–224.
- Muchuweti, M., Birkett, J. W., Chinyanga, E., Zvauya, R., Scrimshaw, M. D., & Lester, J. N. (2006). Heavy metal content of vegetables irrigated with mixtures of wastewater and sewage sludge in Zimbabwe: implications for human health. *Agriculture, ecosystems & environment*, 112(1), 41–48.
- Njoga, E. O., Ezenduka, E. V., Ogbodo, C. G. et al. (2021). Detection, distribution and health risk assessment of toxic heavy metals/metalloids, arsenic, cadmium, and lead in goat carcasses processed for human consumption in South-Eastern Nigeria. *Foods*, 10(4), 798. <https://doi.org/10.3390/foods10040798>
- Park, J. H., Choppala, G. K., Bolan, N. S., Chung, J. W., & Chuasavathi, T. (2011). Biochar reduces the bioavailability and phytotoxicity of heavy metals. *Plant and soil*, 348, 439–451.
- Santos, S., Costa, C. A., Duarte, A. C., Scherer, H. W., Schneider, R. J., Esteves, V. I., & Santos, E. B. (2010). Influence of different organic amendments on the potential availability of metals from soil: A study on metal fractionation and extraction kinetics by EDTA. *Chemosphere*, 78(4), 389–396.

- Ullah, R., Malik, R. N., & Qadir, A. (2009). Assessment of groundwater contamination in an industrial city, Sialkot, Pakistan. *African Journal of Environmental Science and Technology*, 3(12).
- Varrault, G., & Bermond, A. (2011). Kinetics as a tool to assess the immobilization of soil trace metals by binding phase amendments for in situ remediation purposes. *Journal of hazardous materials*, 192(2), 808-812.
- Verheijen, F., Jeffery, S., Bastos, A. C., Van der Velde, M., & Diafas, I. (2010). Biochar application to soils. *A critical scientific review of effects on soil properties, processes, and functions. EUR*, 24099(162), 2183-2207.
- Yang, X., Lu, K., McGrouther, K., Che, L., Hu, G., Liu, X., Shen, L., Huang, H., Ye, Z., Wang, H., 2016b. Bioavailability of Cd and Zn in soils treated with biochars derived from tobacco stalk and dead pigs. *J. Soil. Sediment.* <http://dx.doi.org/10.1007/s11368-015-1326-9>.
- Zimmerman, A. R. (2010). Abiotic and microbial oxidation of laboratory-produced black carbon (biochar). *Environmental science & technology*, 44(4), 1295-1301.

Table 1: Effect of biochar on physico chemical soil attributes.

	Control	1% BC ₄₀₀	3% BC ₄₀₀	1% BC ₆₀₀	3% BC ₆₀₀
pH	7.6	7.7	7.79	8	8.2
EC (dSm ⁻¹)	1.15	1.16	1.2	1.23	1.34
Organic matter (%)	0.45	0.50	0.61	0.65	0.73
Soil texture	Loam	Loam	Loam	Loam	Loam
Cr (mgkg ⁻¹)	3900	3923	3940	3934	3950

Table 2 Extractible content of Cr at equilibrium (24 h), (Q₁) labile fraction, (Q₂) slowly labile fraction, 1/K₁ and 1/K₂ are release time and model validation parameters; SEE (standard error of estimates) and coefficient of fitting (R²).

Treatments	Extractable (24hr)	Q ₁ (%)	Q ₂ (%)	Q ₁ /Q ₂	1/K ₁ (Min)	1/K ₂ (min)	R ²	SEE
Control	1891.66 e	799.46±21.8 3 d	1075.15±20.6 7 c	0.7435	8.46 ±0.01 bc	294.1 ±0.0002 b	0.9959	29.95
1%BC ₄₀₀	2328.33 d	1095.21±72.16 b	1337.57±91.7 9 bc	0.8195	13.75±0.0 14 c	588.23±0.00 04 c	0.9676	106.045 1
3%BC ₄₀₀	2463.33 c	1322.37±80.97 a	1478.08±315.82 b	0.8946	15.22±0.0 12 c	1000±0.0005 c	0.9485	129.385 1
1%BC ₆₀₀	2505.66 b	952.14±51.06 c	1509.93±0.09 5 ab	0.6305	4.65±0.09 5 a	178.57±0.00 05 a	0.9895	62.7388
3%BC ₆₀₀	2828.33 a	1086.32±35.92 b	1757.91±34.9 8 a	0.6179	4.81±0.05 5 ab	196.07±0.00 03 a	0.9958	46.4063