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Sugarcane bagasse-derived biochar reduces the cadmium and chromium bioavailability to mash bean and enhances the microbial activity in contaminated soil

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Abstract

Purpose Remediation of heavy metals by reducing their mobility and bioavailability without removing them from soils is considered to be a cost-effective and an efficient method to address their toxicity for living organisms and soil health. The main objectives of the current study, therefore, were to investigate the potential of sugarcane bagasse biochar in reducing the bioavailability of soil cadmium (Cd) and chromium (Cr) and assessing the impact of biochar application on soil microbial activities and plant growth in metal-contaminated soil.

Materials and methods Air-dried soil was artificially spiked with Cd and Cr metals by using $Cd(NO_3)_2$ and $Cr(NO_3)_2$ solutions. Biochar was homogenously mixed in metal-spiked soil. The experimental spiked soil was categorized as with and without biochar-amended soil. Mash bean crop was used as test plant. After crop harvesting, soil Cd and Cr were extracted by diethylenetriaminepentaacetic acid (DTPA) to estimate the mobility of heavy metals. Furthermore, the plant metal contents, microbial biomass carbon, urease activity, dehydrogenase (DHA) activity, total organic carbon, and plant biomass were determined. The Langmuir adsorption isotherms were studied for Cd and Cr in unamended soil, biochar-amended soil, and biochar only. The electronegative charges of biochar and biochar-amended soil were also measured using the zeta potential.

Results and discussion The results show that the application of biochar to Cr- and Cd-contaminated soil significantly reduced their availability by 85 and 63%, respectively. The application of biochar at 15 g kg^{-1} prominently reduced the extractable Cd contents by 29 and 32% in Cd-contaminated and Cr–Cd-contaminated soils, respectively. The Cr concentration in the plant decreased by 34 and 41% in Cr-contaminated and Cr–Cd-contaminated soil compared with spiked soil without biochar. The Langmuir model achieved the best fit; its isotherm predicted the biochar's maximum adsorption capacity for Cd (0.42 mg g^{-1}) and Cr (0.35 mg g^{-1}). Biochar incorporation in Cd–Cr-contaminated soil significantly increased the microbial activity and mash bean biomass.

Conclusions Our findings indicate that the addition of sugarcane bagasse-derived biochar significantly reduces the Cd and Cr availability in single and co-contaminated soil. In addition, an increase in the microbial activity and plant growth and a significant reduction in the Cd and Cr uptake by mash bean are possible after biochar addition.

Keywords Biochar · Cadmium · Chromium · Immobilization · Sorption isotherms

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1 Introduction

Heavy metal contamination due to anthropogenic activities is a global problem and has multiple negative effects on soil–plant systems. This problem is becoming more severe, especially in developing countries, where untreated waste and sewerage water is widely used for irrigation or is disposed of in fresh water resources (UNIDO 2002; Pollice et al. 2004). In arid and semiarid regions, the fresh water scarcity for irrigation is leading to the increased use of wastewater for crop production (Roohi et al. 2016). The excessive use of such contaminated wastewater generally increases the concentration of heavy metals, such as chromium (Cr) and cadmium (Cd), in soils (Sun et al. 2009). Other causes of heavy metal contamination in soils include the addition of metal-contaminated farmyard manure, sewage sludge, chemical fertilizer, and industry and mine residues (Lu et al. 2014).

High concentrations of heavy metals reportedly reduce the plant productivity and crop yields (Rizwan et al. 2016). Cadmium is a toxic heavy metal, which negatively affects plants by altering physicochemical processes such as transpiration, respiration, photosynthesis, and assimilation (Brunetti et al. 2011; Rizwan et al. 2016). In general, the average contents of Cd in soil range between 0.06 and 1.1 mg kg^{-1} (Kabata-Pendias and Pendias 2001). The Cd contamination originates from mine tailings, fuel combustion, phosphate products, and industrial sludge (Lu et al. 2014). Cadmium enters the food chain when agricultural crops are grown in Cd-contaminated soils or by irrigating the soil with wastewater containing higher concentrations of Cd (Chaney et al. 2005). Chromium is also a significant pollutant of agronomic crops; its concentrations range from 5 to 100 mg kg^{-1}. The critical level of trivalent Cr (Cr^{3+}) in wastewater and soil is 5 mg L^{-1} (Acar and Malkoc 2004). The maximum permissible limits for total and hexavalent Cr (Cr^{6+}) in drinking water are 2 and 0.05 mg L^{-1}, respectively (Park et al. 2004). It has been reported that the presence of Cr in soil could reduce the plant growth by inhibiting several physiological processes such as the root cell division, elongation, ultracellular structural damage due to sensitive tissue collapse of plants, and significant reduction in water uptake by plant roots. Furthermore, Cr exerts stress on the plants' roots to reduce their canopy size and capacity to absorb water by the root hair (Zou et al. 2006).

One of the major approaches for remediation of metal-contaminated soils is the use of soil amendments. Several amendments have been used to decrease the bioavailability of metals in soils and plants by immobilizing them into stable forms (Kumpiene et al. 2008; Shaheen and Rinklebe, 2015). Organic amendments are very efficient to detoxify the effects of heavy metals on soil–plant systems because they are derived from raw biological waste and little pretreatment is required before their application (Park et al. 2011; Yin et al. 2016). Among such organic amendments, biochar, the material produced through pyrolysis of biomass under limited oxygen supply, is widely employed nowadays and has multiple benefits for soils and crops (Xu et al. 2013; Du et al. 2017; Hussain et al. 2017). Biochar is biochemically stable and resistant to decomposition compared with uncharred organic materials and possesses a significant potential to increase the long-term soil organic carbon storage (Lehmann et al. 2011). Biochar can enhance the soil water storage capacity, increase the nutrient availability, and decrease toxic effects of metals (Lehman et al. 2011; Herath et al. 2015, 2017). Lu et al. (2014) reported the decrease of the Cd, Zn, and Pb bioavailability in contaminated soil after biochar application. Bamboo-derived biochar increased the adsorption of Cu, Hg, Ni, Cd, and Cr from soil and water in polluted soils (Park et al. 2011). Biochar reduced the Cd bioavailability by transforming the extractable form of heavy metals into the strongly bound form in the soil (Qiu and Guo 2010). Biochar is a good option for heavy metal stabilization in contaminated soils, which leads to the reduced uptake of heavy metals by plants (Beesley et al. 2011; Lu et al. 2014). Biochar has a higher heavy metal adsorption capacity compared with other biosorbents. The adsorption capacity of biochar depends on the pyrolysis conditions and type of feedstock (Xu et al. 2013; Melo et al. 2016).

The reduced mobility of metals in contaminated soil due to biochar application can also minimize the risk of metal uptake by plants. Applications of biochar reduced the concentration of As, Cd, and Cu in shoots of maize; however, the plant uptake patterns of Pb and Zn were inconsistent (Namgay et al. 2010). In a previous study, Park et al. (2011) suggested that the addition of chicken manure biochar prominently decreases the heavy metal uptake, especially that of Cu and Pb by *Brassica juncea* L. The addition of bamboo and rice straw biochars was effective in increasing the heavy metal immobilization, thus reducing the chances of Cd, Cu, Pb, and Zn uptake by *Sedum plumbizincicola* grown in a severely polluted soil. The increase in the soil pH with biochar amendments decreased metal toxicity, and increased the plant growth of *S. plumbizincicola* (Lu et al. 2014). The recent study reported by Puga et al. (2015) suggested that addition of sugarcane biochar reduced Zn, Pb, and Cd by 54, 50, and 56%, respectively, in mine-polluted soil and prominently reduced plant uptake. Several other studies also suggested that addition of organic and inorganic amendments into Cd-polluted soils significantly reduced its uptake by wheat and promoted the plant growth (Rizwan et al. 2016; Qayyum et al. 2017).

Based on the discussion above and considering a limited knowledge on the effects of sugarcane bagasse-derived biochar on heavy metal mobility and microbial activity in Cd- and Cr-contaminated soil, we performed a pot experiment using mash bean (*Vigna mungo* L.) as test crop in the metal-contaminated soil in order to explore the hypothesis that sugarcane bagasse-derived biochar could help to immobilize the soil heavy metals due to adsorption on its large surface

area. We further hypothesized that Cd and Cr uptake by plants would be reduced conversely to improve soil microbial activity due to positive effects of biochar on soil physicochemical and biological properties. In addition to the pot experiment examining the effects of biochar on the growth and development of mash bean (*V. mungo* L.), metal uptake and immobilization in soil, and changes in the soil biological properties in Cd- and Cr-contaminated soil, the efficiency of biochar in adsorbing Cd and Cr was also assessed through sorption batch experiments and by fitting the data were analyzed by applying to Langmuir sorption isotherms.

2 Materials and methods

2.1 Soil sampling and characterization

A composite surface soil sample (0–15 cm depth) of several kilograms was collected from the research fields of the Department of Soil Sciences, PMAS Arid Agricultural University Rawalpindi, Pakistan (33° 1′ N to 36° 6′ N, 73° 30′ E to 73° 45′ E). After transferring to the laboratory, the sample was air-dried, crushed, sieved through a 2-mm mesh, and stored in plastic bags for further use. A subsample was separated from the composite sample for soil physicochemical analysis before the start of the experiment. The soil pH and EC were measured using a 1:5 (*w*/*v*) soil–water suspension, and readings were taken with automated pH and EC meters, respectively. The soil texture was determined through the pipette method (Lu 1999). Total organic carbon (TOC) contents were measured using the Walkley–Black method (Walkley and Black 1934). Total soil phosphorus (P), nitrogen (N), and potassium (K) contents were measured according to Lu (1999). Cation exchange capacity (CEC) of the soil was measured using the ammonium acetate method at pH 7.0 (Lu 1999). The total soil Cd and Cr concentrations were determined with an atomic absorption spectrophotometer (AAS) after digestion of the samples with the mixture (3:1) of HCl-HNO_3 (Kim et al. 2010). The results related to the soil properties examined are summarized in Table 1.

2.2 Biochar production and characterization

Sugarcane bagasse feedstock samples were collected from the local sugarcane crushing units. The samples were air-dried and crushed to pass through a 10-mm mesh sieve. Biochar was produced by pyrolysis of the bagasse in a ceramic porcelain crucible in the absence of oxygen in a muffle furnace at 500 °C for 2 h (Yuan and Xu 2011). The temperature was gradually increased at a rate of 20 °C min^{-1} until achieving 500 °C and was then kept constant at 500 °C until the pyrolysis of the feedstock was completed.

Table 1 Characteristics of soil and biochar used in the experiment

Property	Soil	Biochar
pH	7.54	7.20
Total organic C (g kg^{-1})	4.20	640.00
Total N (g kg^{-1})	13.40	11.40
Total P (g kg^{-1})	7.21	16.21
Total K (g kg^{-1})	23.52	23.92
CEC (cmol kg^{-1})	10.39	29.39
Total Cd (mg kg^{-1})	0.20	0.03
Total Cr (mg kg^{-1})	2.75	1.65
Ash contents (%)		54

The pH, EC, CEC, and Cd and Cr contents of the biochar were determined using the standard procedures as described above for soil samples. The total C and N contents of the biochar were measured with a CHNS/O analyzer (Perkin Elmer, 2400 II). The results of physicochemical properties of the biochar used in this experiment are listed in Table 1.

2.3 Soil spiking, incubation, and pot experiment

The Cd and Cr contamination levels were developed in 4 kg of soil in plastic pots by spiking it with 50 mg kg^{-1} Cd and Cr using $Cd(NO_3)_2$ and $Cr(NO_3)_2$ solutions, respectively. These Cd and Cr contamination levels were based on the average contamination level in the majority of the heavy metal-contaminated soils in Pakistan (Waseem et al. 2014). Biochar was added to the pots at 15 g kg^{-1} (*w*/*w* basis) and was mixed thoroughly to make a homogeneous soil–biochar mixture. The treatments applied included uncontaminated soil with and without biochar addition (control), Cr-contaminated soil with and without biochar addition, Cd-contaminated soil with and without biochar addition, and Cr–Cd-contaminated soil with and without biochar addition. After metal spiking and biochar addition, the soil pots were incubated for 4 months while maintaining a saturation percentage of 70% (*w*/*v*) and were kept in a constant room temperature at 25 °C. The plant growth experiment was laid out in a completely randomized design with three replicates per treatment. When the preconditioning period was completed, ten seeds of mash bean were sown in each pot and irrigated with distilled water. Commercial chemical fertilizers were used to fertilize with 0.19 g N, 0.11 g P_2O_5, and 0.13 g K_2O per pot in form of urea, calcium superphosphate, and sulfate of potash, respectively. After a 3-month growth period, the plants were harvested to record the plant height, root length, and shoot and root fresh and dry biomass parameters. The soil samples were kept into clean plastic bags and stored at 4 °C until the further analysis. Some parts of the plant and grain samples were oven-dried at 70 °C and were digested before analysis to

measure the Cd and Cr concentrations of the plant biomass following the method described by Kim et al. (2010).

2.4 Soil Cd and Cr concentrations

The diethylenetriaminepentaacetic acid (DTPA) was used to extract the available soil Cd and Cr concentrations using the method described by Lindsay and Norvel (1969). For this, 5.0 g of each sample was extracted with 25 mL of 0.005 M DTPA solution in 50-mL centrifuge tubes. The soil suspensions were shaken for 1 h on an orbital shaker at 150 rpm and then centrifuged, filtered through Whatman filter paper no. 42, and stored in glass vials. The extracts were kept at 4 °C before analyzing the Cd and Cr concentrations using AAS.

2.5 Soil microbial activity analysis

The microbial biomass carbon (MBC) was estimated using the fumigation–extraction method (Brookes et al. 1985). Two 10-g portions of each moist soil were weighed into glass vials. One portion was immediately extracted with 0.5 M K_2SO_4 (1:5 *w*/*v* ratio), and the extracts were frozen after filtration. The second portion of moist soil was fumigated with ethanol-free $CHCl_3$ for 24 h at 25 °C. After the fumigation, the soil samples were extracted with 0.5 M K_2SO_4. Total organic carbon contents of the extracts were analyzed using the Walkley–Black method (Walkley and Black 1934). The difference between the C contents of the fumigated and non-fumigated samples was calculated as the MBC (Brookes et al. 1985).

The soil dehydrogenase activity (DHA) was measured using the protocol described in Alef and Nannipieri (1995). Three grams of moist samples was incubated at 27 °C for 24 h with 3 mL triphenyl tetrazolium chloride (TTC) solution prepared in 0.1 M Tris buffer. After the incubation, methanol was added to extract the triphenyl formazan (TPF) produced by DHA in the soil sample. The solution was filtered through Whatman 42 filter papers, and the absorbance of the extracts was measured at a wavelength of 485 nm using a spectrophotometer.

The soil urease activity was also measured following the method of Alef and Nannipieri (1995). For this, 5 g soil sample was placed into a 250-mL conical flask to which 10 mL of 10% urea solution and 20 mL of citric acid buffer (pH 6.7) were added. The soil samples were incubated at 37 °C for 24 h. Subsequently, the solution was filtered through Whatman 42 filter paper. Three milliliters of filtrate was transferred to a 50-mL volumetric flask, and 20 mL distilled water was added along with 4 mL mixed reagent of phenol and NaOH; 4 mL of sodium hypochlorite solution was added to this mixture, and the final volume including distilled water was 50 mL. The absorbance of the solution was measured at a wavelength of 578 nm using a spectrophotometer.

2.6 Zeta potential determination

Soil samples with and without biochar were also used to determine the zeta potential of the soil and biochar. The soil samples (0.25 g L^{-1}) were used in the presence of 0.01 M $NaNO_3$ electrolyte solution. The pH of the solution was adjusted, ranging from 3 to 5.5, by 0.1 M NaOH and HNO_3. The soil suspension was dispersed ultrasonically for 1 h and kept under sonication for 24 h. The zeta potential values of all solutions were estimated with a zeta potential analyzer (Zeta Plus 90, Brookhaven Instruments Corporation, USA; Jiang et al. 2008).

2.7 Heavy metal contents in the plant

The harvested plant parts were carefully washed with tap water and rinsed two to three times with distilled water to remove the dust particles, and then oven-dried at 60–70 °C for 48 h. The dried tissues of mash bean were ground to powder using an electric mill. The subsamples of the plant tissues (0.20 g) were digested with a mixture of $H_2SO_4/HClO_4$ (2:1 ratio *v*/*v*) to determine the Cd and Cr concentrations using AAS (Kim et al. 2010).

2.8 Batch adsorption study of incubated soil

For the batch sorption equilibrium study, the soil was incubated for 30 days after addition of 1.5% (*w*/*w*) of biochar. A triplicate soil sample of 1.0 g was weighed into 50-mL polythene bottles. Each bottle also contained 25 mL of $Cd(NO_3)_2$ or $Cr(NO_3)_2$ test solutions of concentrations ranging from 1 to 50 mg L^{-1}. The background electrolyte of 0.01 M $NaNO_3$ was used in the metal solution to maintain ionic strength.

The pH of the solutions was adjusted to 5.0 using HCl and/or NaOH. The mixture of the soil and metal suspension was shaken on an orbital shaker for 24 h at 120 rpm and 25 °C. Subsequently, the suspension was centrifuged at 4500 rpm and the supernatant was collected from each tube, filtered through a 0.45-µm qualitative filter paper, and analyzed with AAS. To determine the capacities of the soil to adsorb Cd and Cr, the Langmuir model was employed to fit the data.

$$Ci\Big/x\Big/m = 1\Big/kb + c\Big/b \tag{1}$$

where Ci is the concentration of Cd or Cr in the symmetry solution (mg L^{-1}); x/m is the amount of Cd and/or Cr sorbed (mg g^{-1}) by the soil; b is the adsorption maximum, also denoted Q_m based on the conventional Langmuir equation; and k is the bonding energy coefficient (mg L^{-1}) described in Syers et al. (1973).

2.9 Statistical analysis

The analysis of variance (ANOVA) and Duncan multiple range tests ($p < 0.05$) were used to determine the significant results of all tested amendments. The statistical variations of the presented data were expressed with the standard deviation and $p < 0.05$ significance. All statistical analysis was performed using XLSTAT 2010 (Addinsoft) software.

3 Results

3.1 Soil and biochar characteristics

The basic physicochemical properties of the cropland soil used in the experiment are presented in Table 1. The soil was slightly alkaline (pH 7.54), and the Cd (0.2 mg kg^{-1}) and Cr (2.75 mg kg^{-1}) concentrations were below the maximum permissible limits. Other soil properties were found to be commonly associated with alkalinity, such as TOC and soil CEC, which were 4.20 g kg^{-1} and 10.39 cmol kg^{-1}, respectively. The soil nutrient status, as indicated by total N (13.40 g kg^{-1} soil), total P (7.21 g kg^{-1} soil), and total K (23.52 g kg^{-1} soil), suggests that the nutrient status was poor and supplement nutrients were required to achieve optimum plant growth in the soil.

Table 1 also shows the basic properties of biochar used in the experiment. The heavy metal concentrations, especially Cr and Cd, in the sugarcane-derived biochar were very low compared to those in the soil; hence, the Cr and Cd concentrations added to the soil by biochar application were negligible. The pH of the biochar was 7.20, implying the potential for a slight decrease in the soil pH when added into soil to ameliorate the heavy metal toxicity. Biochar has important chemical characteristics, that is, a high CEC value of 29.39 cmol kg^{-1} and a high TOC of 640 g kg^{-1}. The total N, P, and K contents in the biochar sample were 11.40, 16.21, and 23.92 g kg^{-1}, respectively.

3.2 Impact of biochar on the soil pH

The soil pH significantly ($p < 0.05$) changed because of the addition of biochar in Cd, Cr, and Cd–Cr-contaminated soils. The addition of biochar (15 g kg^{-1}) to metal-contaminated soil showed a slight increment in the soil pH by 0.34 units compared to the control sample without biochar addition (non-amended contaminated soil) (Fig. 1).

3.3 Impact of biochar on the soil Cr and Cd availability

The addition of biochar significantly ($p < 0.05$) reduced the plant available Cr and Cd contents in the soil (DTPA-extracted; Fig. 2). The biochar application reduced the availability of Cr and Cd metals in the soil by 85 and 62.5%, respectively, compared with Cr- and Cd-spiked soils without biochar addition. The Cr availability was lower in Cr–Cd-contaminated soil compared to Cd in both treatments, i.e., with and without

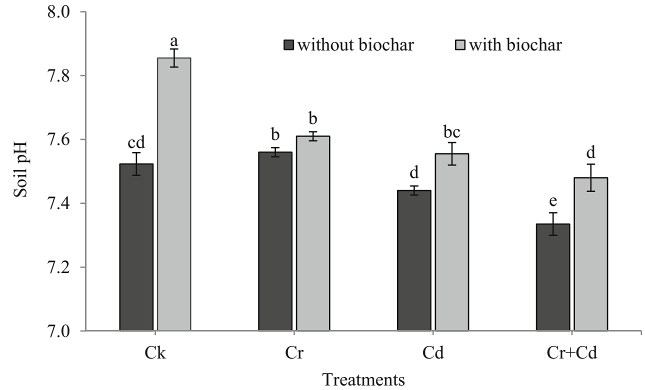

Fig. 1 Effect of biochar on soil pH in the Cr, Cd, and Cr–Cd-contaminated soil. All values are averages of three replications. The *error bars* are the standard deviation of the means ($n = 3$). *Bars with different letters* differ significantly from each other at $p < 0.05$. *Ck* control (non-contaminated soil)

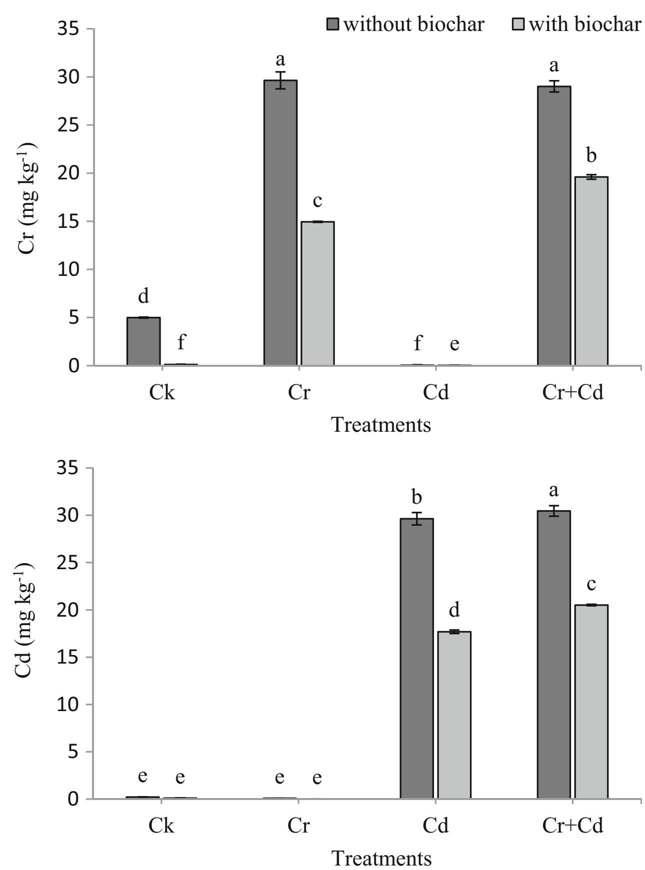

Fig. 2 Effect of biochar on the Cr and Cd concentrations (mg kg^{-1}) in soil with Cr, Cd, and Cr–Cd contamination. All values are averages of three replications. The *error bars* are the standard deviation of the means ($n = 3$). *Bars with different letters* differ significantly from each other at $p < 0.05$. *Ck* control (non-contaminated soil)

biochar. According to our results, all treatments (with and without biochar addition) significantly differed from the control soils in terms of the availability of Cd and Cr.

3.4 Impact of biochar on the biochemical properties of Cr- and Cd-contaminated soils

The changes of the soil TOC, MBC, DHA, and urease activity after mash bean growth are shown in Table 2. All treatments showed significant ($p < 0.05$) variations compared with the control. All treatments with biochar application exhibited a higher TOC than the treatments without biochar application. The highest TOC (10.23 g kg^{-1}) was recorded in the control treatment with biochar application, which was 40.7% higher than the control treatment without biochar application. The lowest TOC contents were recorded in Cd- (4.09 g kg^{-1}) and Cd–Cr-contaminated (4.01 g kg^{-1}) soil.

A lower amount of MBC (130.68 mg kg^{-1}) was observed in the treatment of the Cd–Cr-contaminated soil, while the maximum amount of MBC (168.46 mg kg^{-1}) was observed in Cr-contaminated soil amended with biochar (Table 2). The biochar application increased the MBC by 16.8 and 13.5% in Cr-contaminated and Cd-contaminated soil, respectively, compared with Cr- and Cd-contaminated soil without biochar.

Different treatments significantly affected the urease activity; the highest urease activity was observed in the control sample with biochar application (632.51 μg NH_4^+-N g^{-1} soil h^{-1}), which was 4.75% higher than that of the control sample without biochar application. The lowest urease activity was noticed in the Cd–Cr-contaminated soil without biochar amendment. The application of biochar enhanced the urease activity by 12, 27, and 24% in soils contaminated with Cr, Cd, and Cr–Cd, respectively compared to the similar treatments without biochar.

A significant decline in the activity of dehydrogenase (DHA) was observed in Cr- and Cd-contaminated soil without biochar treatment (Table 2). The highest DHA (83.62 μg TPF g $soil^{-1}$ h^{-1}) was observed in the control sample with biochar application, while the minimum DHA (47.63 μg TPF g $soil^{-1}$ h^{-1}) was observed in soil contaminated with Cd without biochar application.

3.5 Effects of biochar on plant growth

The data regarding the effects of biochar application on the mash bean plant growth in Cr- and Cd-contaminated soil (Cr, Cd, and Cr–Cd) is presented in Table 3. The maximum plant height (43.01 cm) was recorded in the control soil with biochar application. The plant height significantly decreased ($p < 0.05$) in soils contaminated with Cd, Cr, or the combination of both. The minimum plant height was recorded in Cr–Cd-contaminated soil (15.11 cm) without biochar application. It was noticed that the application of biochar to Cr- or Cd-contaminated soil significantly enhanced the plant height.

The data recorded for the root and shoot biomass under different treatments with and without biochar application is also presented in Table 3. The different treatments show significant differences. The maximum root and shoot fresh and dry biomass weights ranged from 2.67 to 7.0 and 1.48 to 5.3 g, respectively. The plant root and shoot biomass yields were higher in biochar-amended Cd- and Cr-contaminated soil compared with unamended contaminated soil.

3.6 Biochar effect on the metal concentrations in the plant

The concentration of Cd and Cr in plant tissues of mash bean varied significantly ($p < 0.05$) for soils with and without biochar treatments (Fig. 3). A substantial decline in the uptake of Cr and Cd was observed with the addition of biochar. The addition of biochar reduced the Cr concentration by 33.5 and 41.29% in Cr-and Cr–Cd contaminated soils, respectively, while the Cd concentration decreased by 28.74 and 32% in

Table 2 Effects of treatments in the presence and absence of biochar on the total organic carbon (TOC), microbial biomass carbon (MBC), dehydrogenase activity (DHA), and urease enzymatic activity

Treatments	TOC (g kg^{-1})		MBC (mg kg^{-1})		DHA activity (μg TPF g^{-1} soil h^{-1})		Urease activity (μg NH_4^+-N g^{-1} soil h^{-1})	
	Without biochar	With biochar	Without biochar	With biochar	Without biochar	With biochar	Without biochar	With biochar
Control	6.60b	10.23a	163.35b	224.13a	67.39b	83.62a	603.80ab	632.51a
Cr	5.03cd	7.02b	140.13de	168.46b	54.51d	60.80c	511.58c	583.79b
Cd	4.08d	6.08bc	134.90e	156.02bc	47.63f	51.23e	419.54d	576.83b
Cr + Cd	4.01d	6.34b	130.68e	148.90cd	42.90g	50.19e	385.43e	512.45c

The values are the means of three replicates. The means for each parameter with different letters significantly differ from each other at $p < 0.05$

Table 3 Effects of treatments in the presence and absence of biochar on the plant height and fresh and oven-dry biomass of mash bean

Treatments	Plant height (cm)		Shoot weight				Root weight			
			Fresh weight (g)		Dry weight (g)		Fresh weight (g)		Dry weight (g)	
	Without biochar	With biochar	Without biochar	With biochar	Without biochar	With biochar	Without biochar	With biochar	Without biochar	With biochar
Control	37.62b	43.01a	5.81b	7.08a	4.30b	5.30a	1.60b	2.30a	0.90b	1.20a
Cr	25.90d	30.02c	3.40d	3.92cd	2.29de	2.61d	0.83cde	1.07c	0.60cd	0.70c
Cd	16.95f	22.70e	2.77e	3.61d	1.73e	2.35de	0.78de	0.98cd	0.40de	0.40e
Cr + Cd	15.11f	22.93e	2.67e	4.33c	1.48f	3.41c	0.76e	0.98cd	0.40de	0.50de

Values are means of three replicates. Means for each parameter with different letters differ significantly from each other at $p < 0.05$

Cd- and Cr–Cd-contaminated soil, respectively, after amendment with biochar.

3.7 Zeta potential measurement

Positive variations in the zeta potential values were observed with respect to biochar; the surface charges became more negative with increasing pH of the solution (Fig. 4). The biochar showed more negative values (−10.13 to −31.8) with increasing pH (3 to 5.5) compared with other soil amendments due to more oxygen-containing functional groups on its surface.

3.8 Adsorption isotherm of Cr and Cd of biochar and biochar-amended soil

Langmuir isotherm and Freundlich models were used to predict the behavior of Cd and Cr sorption in the soil after biochar amendment. However, the data of the Langmuir model showed the best fit; therefore, only these results are presented in this study (Fig. 5). The data pertaining to Cd and Cr adsorption maxima (Q_m) under different treatments are presented in Table 4. The Langmuir model predicted that the highest value of adsorption capacity, denoted as Q_m, is 0.42 mg g^{-1} for the adsorption of Cd onto biochar. While, the minimum value of Q_m is 0.30 mg g^{-1} for soil used for the Cd adsorption study. Soil amended with biochar showed a Q_m value of 0.35 mg g^{-1}. The results indicated that the Langmuir-predicted adsorption maximum Q_m of biochar for Cd adsorption is 28.75% higher than that of soil. The regression constant (R^2) value for Cd adsorption obtained from the Langmuir adsorption isotherm was 0.99 for biochar and soil amended with biochar, while it was 0.96 for soil alone.

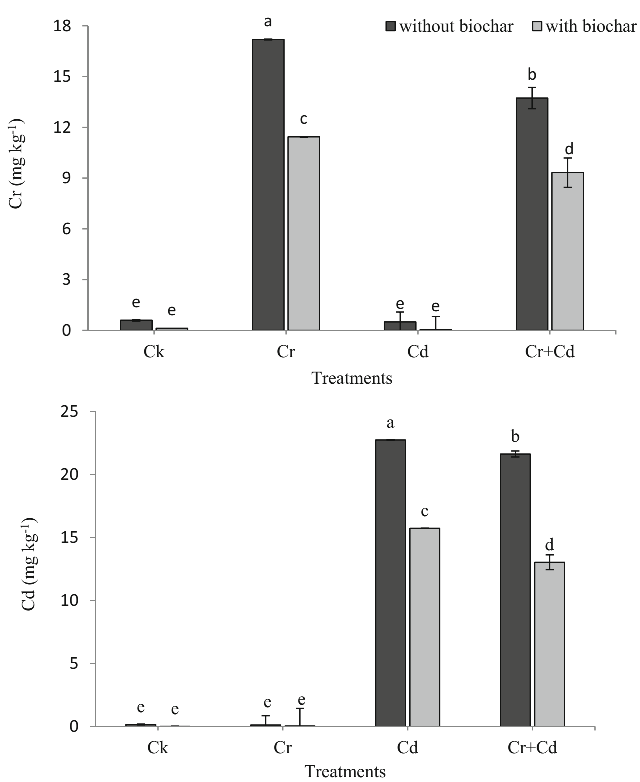

Fig. 3 Effect of biochar on the Cr and Cd concentrations in mash bean tissues. All values are averages of three replications. The *error bars* are the standard deviation of the means ($n = 3$). *Bars with different letters* differ significantly from each other at $p < 0.05$. *Ck* control (non-contaminated soil)

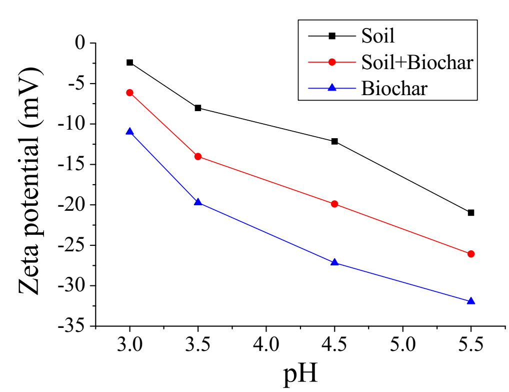

Fig. 4 Effect of biochar on the zeta potential of the soil particles at a pH between 3 and 5.5

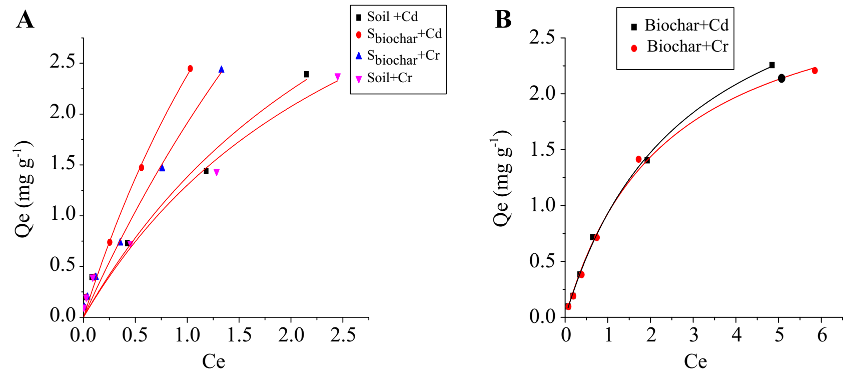

Fig. 5 Langmuir adsorption isotherm of cadmium (Cd) and chromium (Cr) for biochar (BC)-amended soil, soil alone (**a**), and BC only (**b**)

Biochar exhibited the highest value of Q_m (0.35 mg g^{-1}) for the adsorption of Cr, whereas the minimum value (0.19 mg g^{-1}) of Q_m was observed for Cr adsorption onto soil. Soil amended with biochar has a Q_m value of 0.34 mg g^{-1}. Biochar showed a 45.71% higher value of Q_m compared with soil. The regression constant (R^2) value of Cr adsorption obtained from the Langmuir adsorption isotherm was 0.96, 0.98, and 0.99 for biochar, soil amended with biochar, and soil alone, respectively.

4 Discussion

4.1 Biochar influence on the soil pH

In the present study, we evaluated the efficiency of sugarcane bagasse-derived biochar with respect to soil chemical properties, soil Cd and Cr availability, soil microbial activities, plant growth, and metal uptake in contaminated soil. Incorporation of biochar significantly increased the soil pH after the harvest of leguminous crop (mash bean). Based on the results, the soil pH increased by ~1–2 units compared with untreated soil. These results are in agreement with that of Shaheen and Rinklebe (2015) who also reported that the soil pH increased up to 0.66–1.82 units due to the addition of 0.5 and 1.5% biochar, respectively, because of the high alkalinity of biochar. According to our findings, biochar has the highest ash contents, which might be responsible for the increase of the soil pH. Our results are consistent with that of Yuan and Xu (2011) who reported that the soil pH prominently increased due to the addition of biochar because of the high mineral ash contents and oxygen-containing functional groups on the biochar surface. It was found that during pyrolysis of organic biomass that contains some basic substances, such as alkali and alkaline earth metals, some essential plant nutrients (S, N, P, and K) and macronutrients (Ca^{2+} and Mg^{2+}) could be changed into compounds of carbonates, oxides, and hydroxides, which might explain that biochar is a liming material increasing the soil pH (Houben et al. 2013).

Table 4 Maximum adsorption capacity derived from the Langmuir model for Cd and Cr sorption onto biochar alone, soil treated with biochar, and soil alone

Treatments	Cd		Cr	
	Qm (mg g^{-1})	R^2	Qm (mg g^{-1})	R^2
Biochar	0.42	0.99	0.35	0.99
Soil + biochar	0.35	0.99	0.34	0.97
Soil	0.30	0.96	0.19	0.96

4.2 Biochar effect on the soil Cd and Cr availability

The DTPA-extractable fractions of Cd and Cr contents in the soil were immobilized by sugarcane-derived biochar over the 4-month study. Compared with untreated soil, the biochar addition to Cd- or Cr-contaminated soil prominently reduced the DTPA-extractable fractions of Cd and Cr by ~40.39 and 49.56%, respectively. This reduction in the availability of heavy metals in soil is possibly due to the increase of the soil pH (Fig. 1) as the biochar was applied to polluted soil. Another reason for the heavy metal immobilization might be the increased soil adsorption capacity due to the development of new exchange sites in biochar-amended soils (Namgay et al. 2010). This is also evident from our results of Langmuir adsorption isotherms. Similar results were observed by Houben et al. (2013) who suggested that the addition of biochar increases the soil pH, which might reduce the heavy metal extractability from soil by providing new sites for heavy adsorption on biochar-amended soils. However, in our study, increase in soil pH was not always significant in biochar-amended soil. Biochar generally has a high porosity, greater surface area, CEC, and numerous negative surface functional groups that play vital roles in reducing the heavy metal mobility through adsorption and precipitation (Lu et al. 2014; Ahmad et al. 2017).

Our results are in agreement with the findings of Qiu and Guo (2010) and Yang et al. (2017) who reported that biochar stabilizes heavy metals in contaminated soils and improves the quality of the contaminated soil by reducing the heavy metal

uptake in crops. Beesley et al. (2010) found that the concentration of Cd significantly decreases during 55 days due to the application of biochar derived from woody material; however, the concentration of Cu in the pore water was much greater than that of the controlled soil.

4.3 Biochar effect on the soil microbial activity

Soil microorganisms play a vital role in soil organic matter decomposition to improve soil nutrient status, soil fertility, and crop productivity (Murrieta et al. 2006). In the present study, differences in the soil microbial biomass carbon and soil dehydrogenase activity (DHA) were observed in Cd- and Cr-contaminated soil with and without biochar application. Based on our results, the soil microbial biomass significantly decreased in metal-contaminated soil, which might be due to unfavorable environment in polluted soils that may release a major portion of carbon as CO_2, and a small portion was remained as organic substrate for microorganisms (Jiang et al. 2003). There are several other mechanisms that might explain the microbial activity reduction in polluted soils. Firstly is the decrease of the CO_2 production under heavy metal contamination due to the reduction of the substrate availability; secondly, the highest concentration of heavy metals strongly inhibits the microbial activity (Murrieta et al. 2006).

We could suggest that the significant increase in microbial activity in our study in biochar-amended soils might be due to the presence of readily available C as substrate and the breakdown of existing carbon after biochar incorporation. These observations were in accordance with Laird et al. (2010) who concluded that addition of biochar significantly increased available soil organic C due to high C contents of biochar that may have the ability to promote microbial activity acting as C substrate. Similarly, Skáodowski et al. (2006) also concluded that organic carbon is mainly responsible for binding heavy metals in metal-contaminated soil. The increase in TOC due to biochar application might be responsible for the reduction of the content of available metal elements as a result of the complex formation between free ions of heavy metals and biochar.

Based on the present results, the soil pH is a key factor involved in the heavy metal reduction in soil after biochar incorporation, which might promote the organic matter degradation and positive increase in the microbial biomass. Similar results were observed by Stewart et al. (2013) who reported that the addition of biochar to soils induces a soil pH increase and also enhances the soil carbon decomposition rate and soil aeration because of the sufficient oxygen supply. Our results showed a significant increase in MBC with biochar addition; sugarcane biochar has the highest TOC contents, which might have played a positive role in the carbon mineralization of the soil. These results are in agreement with the findings of Wu et al. (2015) who proposed a linear relationship between microbial biomass and biochar application because MBC correlates with TOC, which is a substrate for microbial growth. It was found that biochar has a macroporous and microporous structure and a greater CEC that enables it to release nutrients into the soil system, which might be useful for the enhancement of the substrate that provides a microbial habitat in polluted soils (Lehman et al. 2011). Similar results were observed by Prabha et al. (2013) who evaluated the impact of biochar on soil organic C contents. Moreover, the addition of biochar with organic amendments, such as compost and chemical fertilizer, resulted in an increased MBC.

The enzyme activity in metal-contaminated soil is also an indicator for microbial activity that constantly varied with biochar amendments. It could be demonstrated that the addition of biochar (50 mg kg^{-1}) increases the soil urease activity due to two possible reasons. The main reason is that the addition of biochar enhances specific enzymes, which are related to N utilization in contaminated soil (Bailey et al. 2011). The reduction of extractable Cd and Cr in contaminated soil is another reason for the soil urease activity increase when sugarcane biochar was added. Similarly, the activity of dehydrogenase is very sensitive to Cd pollution (Sardar et al. 2007). Ameloot et al. (2013) suggested that application of biochar has a positive impact on the DHA, depending upon on various biochar production temperatures. In our study, biochar prepared at 500 °C also enhanced the DHA. Similar to our findings, Sopeña and Bending (2013) found that the dehydrogenase enzyme activity was enhanced manifold in biochar-amended soil compared with soil without biochar application.

4.4 Biochar effect on plant growth

Based on the literature, several studies have reported that heavy metal stress decreases the plant biomass such as in wheat (Rizwan et al. 2016) and spinach (Younis et al. 2016). The reduction of the biomass might be due to metal-induced reduction of the plant's essential nutrient uptake and ultracellular structural changes in plant species (Rizwan et al. 2016). In the current study, it was noticed that the application of biochar prominently enhances the plant biomass in metal-contaminated soil. The increase in biomass production might be due to the availability of more organic carbon and high water retention in the biochar-amended treatments. Other factors responsible for these positive changes in plant parameters may be the changes in the soil pH and reduction in the Cd and Cr mobility and bioavailability. Similar results were observed by Younis et al. (2016) who reported that the addition of biochar to soil (5%) can increase the plant fresh and dry biomass and plant height compared with the respective Cd- and Cr-spiked soil without biochar addition.

The application of biochar to Cr- and Cd-contaminated soil significantly enhanced the plant height. These results are in accordance with Van Zwieten et al. (2010) who reported that

sludge material-derived biochar applied at 10.0 t ha^{-1} increased the plant height by up to 31–40%. Carter et al. (2013) applied rice husk biochar as potting medium and found an increase by 32% in the biomass of root and shoot; about 36% in plant length and number of leaves in all the cropping systems compared with other treatments during which no biochar was added. It was found that the addition of biochar to metal-polluted soils increases the nutrient supply and nutrient use efficiency, which might be beneficial for the nutrient uptake and increase in plant biomass (Lehman et al. 2011).

The highest plant root and shoot biomass yield was observed in biochar-amended Cd- and Cr-contaminated soil compared with unamended contaminated soil. Our results are supported by Matovic (2010) who reported that the optimal addition of biochar to agricultural soil ranges from 1 to 5%. Both chicken manure and green manure biochars significantly improved the Indian mustard shoots and root biomass, which is ascribed to the decrease of the metal toxicity and increased nutrient availability to soils and plants (Matovic 2010).

4.5 Biochar effect on Cd and Cr contents in plants

The plant tissue concentration of Cd and Cr showed a different behavior in biochar-amended soil compared to untreated soil. In the present results, biochar addition significantly reduced the Cd and Cr concentration in plants by 28.73 and ~33.50%, respectively, compared with unamended soil. This reduction of the Cd and Cr concentration in plants is also strong evidence for the reduction in DTPA-extractable Cd and Cr in soil after biochar incorporation, which might be the main reason for the lowest adsorption of heavy metals by mash bean tissues. These results are consistent with previous studies of Namgay et al. (2010) and Park et al. (2011). They indicated that the addition of biochar significantly reduces the heavy metal mobility in soil and renders their uptake by plants. It can be demonstrated that the incorporation of biochar effectively reduced the DTPA-extractable Cd and Cr of the soil solution by inducing stable organic matter complexes with heavy metals and promoting insoluble mineral formation through complexation and precipitation, which might be the reason for the reduction of the heavy metal uptake by plant tissues (Uchimiya et al. 2010; Beesley et al. 2011).

Similar results were observed by Hossain et al. (2010) who revealed that biochar enhances the fixed fraction of heavy metals in soils and reduces the uptake of heavy metals. As the present study was conducted under alkaline soil conditions, Cr and Cd might have been bound to $CaCO_3$; hence, their concentration reduced in plant tissues. These results are in accordance with Lu et al. (2014); they reported that the addition of rice straw-derived biochar prominently reduces the Cd uptake, by up to 20%, by *S. plumbizincicola* due to the liming effect. They also showed that biochar-amended soil reduces the Cd uptake by *S. plumbizincicola*, which might be due to its adsorption on the biochar surface. The increase of the surface adsorption and precipitation of heavy metals as insoluble mineral phosphates are also possible mechanisms for heavy metal reduction in soil and plant tissues due to biochar addition (Lu et al. 2014).

4.6 Cd and Cr adsorption isotherm and mechanism

The data with respect to Cd and Cr adsorption onto biochar and soil were fitted with the Langmuir isotherm. The results indicate that biochar-amended soil has a higher adsorption compared with metal-spiked soil without biochar. The Cd and Cr adsorption capacity (Q_m) in biochar-amended soil increased by 0.35 and 0.34 mg g^{-1}, respectively, compared with the control soil (0.3 mg g^{-1}), which is similar to results in Jiang et al. (2012) who reported that the adsorption of heavy metals increases in biochar-amended soil. The Cd and Cr adsorption on the sugarcane-derived biochar surface increased approximately one to two times compared with soil with and without biochar. These findings suggest several reasons for the increase in the Cd and Cr adsorption by biochar and biochar-amended soil. The soil pH increases due to the application of biochar, which might also increase the sorption of Cd and Cr on the biochar surface. Biochar develops surface functional groups, such as aromatic OH^- and carboxylic-C, during the oxidation reaction in biochar, which results in the increased adsorption of metals on the surface of biochar.

The addition of biochar induced a negative surface charge with increasing pH, which was confirmed by the zeta potential. The zeta potential of biochar was more negative, from −10.13 to −31.08 mV, at a pH of the solution ranging from 3 to 5.5 (Fig. 4), suggesting that the surface charge in these pH ranges is more negative. This might be the main reason for the higher adsorption in biochar-amended soil. These results point out that biochar surface charges are negative at all pH levels; the zeta potential becomes more negative with increasing pH of the solution. Biochar amendments to soils could increase the protonation and deprotonation of biochar surface functional groups, which creates the net charge of colloidal particles in the soil solution providing an electric double layer that enables the biochar to increase the heavy metal adsorption (Li et al. 2016). The zeta potential values confirm the biochar surface electronegativity due to the presence of a wide range of functional groups such as COO −, COH, and OH (Li et al. 2016). Furthermore, Li et al. (2016) concluded that a more negative charge on the biochar surface could induce more surface adsorption.

These results are in accordance with Jiang et al. (2012) who observed zeta potential changes towards negative values after biochar incorporation. Therefore, the Cd electrostatic adsorption increased with biochar application. On the other hand, the organic matter content and high CEC of biochar might play key roles in surface adsorption. Our results are also in agreement with that of Kumpiene et al. (2008) who suggested

that the addition of biochar increases the soil pH and CEC, which contribute to the enhancement of heavy metal adsorption on the surface. Another reason might be the increase in oxygen-containing functional groups on the biochar surface with increasing soil pH; therefore, the adsorption of positive Cd and Cr ions increased due to the force of attraction. Similar results were reported by Yuan and Xu (2011) who indicated that biochar contains high amounts of functional groups (e.g., −COO and –OH), which could form surface complexes with Cd and Cr and enhance the specific adsorption of Cd and Cr by soils with biochar addition. Therefore, this is the main reason for the increase in the surface adsorption of heavy metals by biochar-amended soil. In addition, the highest biochar pH value plays a vital role in increasing negative charges on soil and biochar surfaces, which enables the entrapment of heavy metal cations on their surface and promotes the adsorption mechanism (Houben et al. 2013).

Lu et al. (2014) also suggested that the high pH, CEC, microporous structure, and excess of soluble salts on the biochar surface increase the heavy metal immobilization through precipitation and surface adsorption. It was found that the heavy metals are bound to carbonates and organic matter after biochar incorporation, which increases the adsorption process due to metals building bonds with oxygen-, carbon-, and nitrogen-containing functional groups such as $CdCO_3$ (Park et al. 2011).

5 Conclusions

The efficiency of sugarcane bagasse-derived biochar to adsorb Cr and Cd, immobilize heavy metals (Cd and Cr) in soil, and reduce the metal concentration in mash bean was tested in a pot experiment. The results revealed that the application of biochar at 1.5% rate (*w*/*w*) significantly improved the biochemical properties of soil such as TOC, MBC, DHA, and urease activity not only in single contaminated soil with Cd or Cr but also under mix contamination of Cr + Cd. The DTPA-extracted soil Cd and Cr contents were reduced by 62.5 and 85%, respectively, due to biochar application, compared to treatments without biochar application. Biochar application also significantly increased the plant growth parameters. The Cr and Cd concentrations in the plant tissue were also reduced in Cr, Cd, and Cr–Cd-contaminated soils with biochar application compared with non-amended soils. The Langmuir isotherm predicted that the biochar showed maximum adsorption capacity for Cd and Cr, followed by soil–biochar and soil. Therefore, it can be concluded that the production of biochar from sugarcane bagasse waste and its application to remediate the Cd- and Cr-polluted soil is an effective remediation strategy to restore the contaminated soil for better crop production both by improving biochemical conditions and reducing metal availability. However, findings of this pot study need to be further validated from field experiments on soil under multiple-metal contaminations and using biochar developed from a wide variety of other feedstocks available.

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