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Effectiveness of corn stalk biochar in amending the contaminated soil attributes and enhancing the sustainable grass growth

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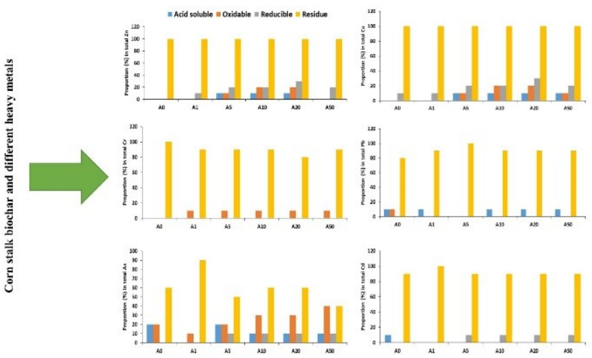
Graphical abstract



Abstract

It is important to rapidly amend the hostile rural soil fertility and quality to develop green land verdure. In this research, cornstalk-derived biochar was added (sequence proportions 0, 1, 5, 10, 20, and 50 % in the mass ratio) into hostile rural soil and then the grass was grown in the pots. The findings indicated that the biochar addition caused substantial enhancement in soil black carbon, organic carbon total nitrogen, available potassium, and phosphorus by more than 4.6, 1.7 1.6, 0.3, and 4.7 times, correspondingly. Grass dry matters (DM) enhanced proportionally with enhancing the quantity of applied corn stalk biochar (69%) owing to enhancement in plant minerals nutrition. Treatment of biochar highly enhanced the total quantities of the soil's heavy metal contents. However, 36 to 90 % of heavy metal contents in treated soil were concentrated in residual fractions with lower bio-availability. Thus, the accumulation of heavy metal contents in the grass above-ground biomass was greatly decreased through biochar application. Our findings showed that corn stalk-derived biochar could be suggested in hostile rural soil as soil ameliorates at an amount of 50%. Conversely, the environmental hazard due to the heavy metals accumulation in the soil treated by corn stalk biochar should be sensibly considered.

Keywords: Biochar, corn stalk, dry matter, grass, heavy metals

1. Introduction

Rural soils are the most hostile soils, typically containing concrete, plastic, parent constituents, and bricks, usually, it is poor fertility and is structure-less. Generally, in this soil difficult to develop vegetation, and expensive to preservation of greenery as well (Chen *et al.* 2020). Biochar is an organic residue prepared under the absence of oxygen, resulting in a porous structure, and lower-density C-enrich substances, which have fascinated and enhanced tending from researchers owing to its advantages as a soil improvement (Reyhanitabar *et al.* 2020). Heightening the information has exposed that the biochar treatment notably affects the biological and physiochemical attributes of soil. Biochar is a carbon-rich material that can be used not only as a renewable fuel but also as an additive for the improvement of soil quality (Ali *et al.* 2023; Raza *et al.* 2023). The nature of carbon structures is the key reason for their high stability. The most pronounced chemical difference between biochar and other organic matter is a much higher proportion of aromatic C and condensed aromatic structures, in contrast to other aromatic structures of soil organic matter, such as lignin (Tomczyk *et al.* 2020). The lower density, as well as porous structures of the biochar, enables decreased bulk density while increasing the soil permeability, availability, and aeration (Dong *et al.* 2013; Hossain *et al.* 2015; Awad *et al.* 2021). Numerous functional groups on the surface of biochar lead to improvement of nutrient use efficacy and cation exchange capacity and a decrease of contaminants mobility in polluted soil (Dong *et al.* 2013; Hossain *et al.* 2015). The substantial liming effects usually decrease the soil acidity together with reducing the actions of Mn2+ Al2+, and other heavy metal contents. Even crop yield, for example, cereals, fibers, tubers, and roots can be expressively improved through biochar addition in temperate, sub-tropical, and even tropical areas (Luo *et al.* 2011). Moreover, biochar soil addition can increase the soil C pools and decrease the emission of nitrous oxide and methane. Most agricultural wastes including corn stalks can be applied as raw material for generating biochar by the pyrolysis mechanism (Dong *et al.* 2013).

Conversely, it is unknown, whether corn stalk biochar can be added to rural soils and amend soil features and their fertility. For this work, corn stalks were collected from an agriculture farm near Khanewal district, Pakistan. The objectives of our research were (i) to determine the consequences of corn stalk-derived biochar on rural soil traits and the growth of grass (ii) also examine the heavy metals accumulation in soil and grass (iii) to measure an appropriate rate of corn stalk biochar addition in rural soil.

2. Materials and methods

2.1. Preparation of corn stalk biochar

The collection of corn stalks for the production of biochar from an agriculture farm located in Khanewal. The biochar was prepared at 500 °C for 4 h. The prepared biochar had the following properties given in Table 1.

2.2. Soil

The rural soil was taken from a soil layer of 15–35 cm in a rural area of Khanewal district Pakistan. The soil had the following attributes given in Table 2: The heavy metals levels were shown in Table 3. Except for cadmium, all the metals found were lower concentrations than WHO, national, and US-EPA limits.

Table 1. Physiochemical attributes of prepared biochar

pH	EC (µS cm^{-1})	C (%)	H (%)	O (%)	N (%)	AVP (mg kg^{-1})	AVK (mg kg^{-1})
8.61	763.81	14.28	0.69	3.39	1.67	193.17	11798.14

EC= Electrical conductivity, AVP= available phosphorus, AVK= available potassium

Table 2. Physiochemical properties of collected soil

pH	EC (µS cm^{-1})	SOC (g kg^{-1})	BC (g kg^{-1})	TN (g kg^{-1})	AVP (mg kg^{-1})	AVK (mg kg^{-1})
8.32	156.67	3.48	0.59	0.31	7.71	63.31

SOC= soil organic carbon, BC= black carbon, TN= total nitrogen

Table 3. Concentration and Fractions of different heavy metals in the soil (mg kg^{-1}) and the environmental quality limits for soils (WHO, USEPA, and Pakistan)

Fractions	Cu	Pb	Cd	As	Cr	Zn
Oxidizable	0.56	0.08	0.00	0.43	0.79	0.39
Acid-soluble	0.02	0.42	0.01	0.00	0.09	0.64
Reducible	0.00	0.13	0.03	0.14	0.01	1.09
Residue	30.04	13.04	1.06	3.04	30.38	47.02
Sum	30.62	13.67	1.1	3.61	31.27	49.14
WHO	36	85	0.8	20	100	50
US-EPA	75	15	1.0	25	100	140
Pakistan	36	85	0.8	25	100	140

2.3. Pot experiments

Portions of the 3 kg soil were uniformly added with corn stalk-derived biochar (0%, 1%, 5%, 10%, 20%, and 50%; labeled as A0, A1, A5, A10, A20, and A50, correspondingly) and urea (56.58 mg N kg-1) in clay-ware pots. All biochar treatment rates were evaluated through three replicates. All pots were sown with 0.28 g (around equal to 200 kg g-1) of added grass seeds of *Poa alsodes*, *Poa foliosa*, *Poa douglasii*, and *Poa cusickii* at an equal ratio. All pots were enfolded into a field with a distance of 3 cm to the soil surface and irrigated regularly. The above-ground biomass of the grass was cut, when it grew to around 10 to 25 cm in height, rinsed with de-ionized water, and then dried and put to analyses of heavy metals phosphorus, total N and K. After the trial in mid-November, samples of soils were taken and then examined for EC, pH, soil texture, organic C, black C, heavy metals, available potassium and phosphorus and total nitrogen.

2.4. Analysis

The pH and EC values of the biochar were measured in a mixture with a 1:10 ratio of biochar to water (w/v) by a glass electrode and conductivity meter, respectively. Total C, H, and N were determined by an elemental analyzer, whereas ash was measured according to the method of Yue et al. (2016). Oxygen was calculated by the difference between 100 and the sum of C, H, N, and ash. Total P and K were determined by ascorbic molybdate blue spectrometry and flame photometry respectively, following wet digestion. The total N, P, and K in the grass samples were determined by the Kjeldahl method, ascorbic molybdate blue spectrometry, and flame photometry, respectively, following wet digestion with H_2SO_4-H_2O_2. Heavy metals were measured by inductively coupled plasma spectrometry (ICP) (ICP 6000 SERIES; Thermo Company, Rockford, IL, USA) following digestion with $HClO_4$-HNO_3. Soil texture was determined by the pipette method. The pH value (1:2.5 of soil to water, w/v) was estimated with a glass electrode. The EC (1:5 of soil to water, w:v) was measured with a conductivity meter. Soil organic carbon was determined using the potassium dichromate volumetry method. Total nitrogen was determined using the Kjeldahl method. Available P and K were determined using Olsen's method and flame photometer, respectively. Black carbon was determined by the benzene polycarboxylic acid (BPCA) method. Briefly, 0.5 g of each soil-biochar mixture (< 0.15 mm) was digested with 10 mL of 4 M trifluoroacetic acid (TFA) at 105 °C for 4 h under a pressure of 3 MPa. The residue was collected, dried at 65 °C for 12 h, and then added 2 mL of 65% HNO_3. The mixture was digested at 170 °C for 8 h under a pressure of 3 MPa and then filtered into a 200 mL volumetric flask through ash-free quantitative fiber filter paper. Organic carbon content was determined using a Multi-N/C Analyzer (Analytics Jena). Black carbon content was calculated with a correction coefficient of 2.27. Total heavy metals were measured by ICP/MS following digestion with HCl-HNO_3-$HClO_4$. The acid-soluble, reducible, oxidizable, and residual fractions of the heavy metals were quantified by the Bureau Commune de Reference (BCR) sequential extraction procedure (Yue *et al.* 2016).

2.5. Statistical analysis

All findings are articulated as the mean of three replicates on a dried basis. The difference among all treatments was analyzed through a t-test and the least significant difference (LSD) at α = 0.05.

3. Results

3.1. Basic physiochemical properties of soil

Cornstalk-derived- biochar treatment had no substantial effect on the texture of the soil but altered other soil physicochemical traits (Table 4). The pH ranges of corn stalk biochar treated soils were reduced by 0.06 to 0.66 units but the organic carbon, black carbon, and total nitrogen enhanced by 1.7 to 40 times, 4.6 to 163 times, and 1.6 to 65 times, correspondingly. The BC/SOC proportion enhanced from 0.14 in control soil (A0) to more than 0.28 in biochar-mixed soils. Available K and P in biochar-treated soil enhanced by 0.3 to 8 times and 4.7 to 40 times, correspondingly, equated to those in A0. Enhances of these traits were usually proportional to the biochar addition amount.

Table 4. Electrical conductivity (EC) pH, black carbon (BC), soil organic carbon (SOC), available potassium (K), available phosphorus (P), and total nitrogen (N) in corn stalk biochar-mixed soil after harvesting the grass

Treatments	pH	EC (µS cm^{-1})	SOC (g kg^{-1})	BC (g kg^{-1})	TN (g kg^{-1})	C/N	BC/SOC	P (g kg-1)	K (g kg^{-1})
A0	8.66a	81.69c	3.19e	0.48e	0.32e	9.97b	0.15e	4.79f	76.87f
A1	8.63a	74.59d	8.99de	2.57e	0.73e	12.32a	0.29d	33.03e	104.89e
A5	8.57b	76d	20.79cd	11.43d	2.76d	7.53d	0.55b	81.51d	152.78d
A10	8.44c	76.72cd	38.49c	20.98c	4.78c	8.05c	0.55b	107.67c	217.74c
A20	8.11d	91.48b	69.87b	40.72b	9.11b	7.67d	0.58a	127.34b	357.14b
A50	8e	104.64a	147.84a	69.49a	21.12a	7.00e	0.47c	178.34a	627.45a

Various lowercase letters in the same column show significant differences at (p < 0.05) between treatments

3.2. Heavy metals in soil

Total concentrations of selected heavy metals in corn stalk biochar mixed soils were proportionally enhanced by the mixed biochar ratio (Table 5). Particularly, Cu and Zn increased by a maximum of close to 10 times, while As and Cd by 10 to 47%, and 20 to 80% respectively. Higher than 82% of heavy metals have been in residual fractions in examined soil. The effect of corn stalk biochar on heavy metal fractions differed with the applied biochar amounts and heavy metal contents (Figure 1).

Generally, corn stalk biochar had a significant effect on fractions of Zn and As but a slight effect on other metals. The residual fractions of the Zn and As in corn stalk biochar mixed soils were reduced by 25 % and 100% respectively, in contrast with those in A0. In comparison, fractions of oxidizable, reducible, and acid-soluble, Zn 30%, 35%, and 25%, and As increased by 60 %, 22 %, and 30 %, respectively. These variations were proportional to the applied biochar amount.

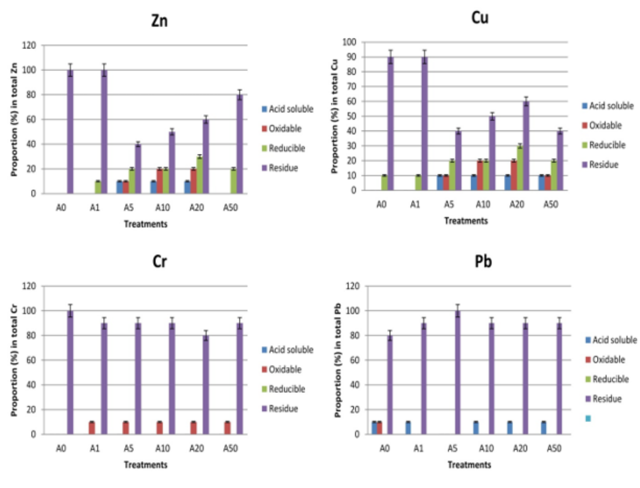


Figure 1. Proportions of various fractions of the heavy metals (Zn, Cu, Cr, Pb, As, and Cd) in corn stalk biochar-treated soils after grass planting.

Table 5. Total amount of selected heavy metals (mg kg^{-1}) in corn stalk biochar-mixed soil after harvesting grass and environmental quality limits for soils (Pakistan, WHO, and US-EPA)

Treatments	Cu	Pb	Cd	As	Cr	Zn
A0	33.47	14.09	1.20	3.48	30.46	56.24
A1	40.21	19.98	1.44	4.18	45.64	87.48
A5	57.34	20.34	1.50	4.25	45.36	121.37
A10	76.13	23.39	1.63	4.39	51.27	212.47
A20	104.51	27.08	1.69	4.57	52.49	315.74
A50	177.34	33.04	1.97	5.47	58.14	598.64
LSD0.05	7.83	2.06	0.16	0.46	4.28	23.97
Pakistan	36	85	0.8	25	100	140
WHO	36	85	0.8	20	100	50
US-EPA	75	15	1.0	25	100	140

3.3. Above-ground dry matters of grass

Corn stalk-derived biochar treatment affected the heavy metal, dry matter, and nutrient content of above-ground grass (Table 6). The dry matter of the grass was uniformly enhanced by the corn stalk biochar addition amount (40 to 130 %, an average of 69%, contrasted with that of control samples). Total K, N, and P contents were enhanced by 9 to 30 % (20% average), 9 to 18 % (4 % average), and 49 to 90 % (68 % average), correspondingly. Accumulation of Arsenic in the above-ground grass was not influenced by biochar application (Table 6). Conversely, the accumulation of cadmium was significantly reduced from 0.14 mg kg-1 in control to 0.03 mg kg-1 in that applied 5% biochar (A5). Biochar treatment at a lower rate (<5%) decreased the accumulations of Pb, Cr, Cu, and Zn in grass biomass, while a higher mixing rate tended to enhance their accumulations. The bioconcentration factors of selected heavy metals, extending from 0 to 0.49, were extremely low (Table 6). Biochar treatment proportionally reduced these factors of total heavy metals, which might indicate that grass did not evenly accumulate the enhanced heavy metals in the biochar-treated soils. Mixing 5% corn stalk biochar tended to cause the lowermost accumulation of heavy metals in the above-ground biomass of grass.

Table 6. Dry matter (DM) and total K, P, and N contents of above-ground grass grown in soil treated with various rates of corn stalk-derived biochar, bio-concentration factors of the heavy metals, and the limits of pollutants in the foods (National, Pakistan)

Treatments	DM	N %	P%	K%	Zn(mg kg)	Cr(mg kg)	Cu(mg kg)	Pb(mg kg)	Cd(mg kg)	As(mg kg)	Biocentration factor					
											Zn	Cr	Cu	Pb	Cd	As
A0	2.49d	2.09b	0.25c	1.15c	31.69b	7.62a	6.12a	2.69c	0.14a	0.0b	0.49	0.18	0.24	0.17	0.0	0.13
A1	4.29b	2.13b	0.39b	1.28b	20.27c	5.37b	3.09c	4.26a	0.10b	0.9a	0.32	0.07	0.14	0.19	0.02	0.09
A5	3.63c	1.87c	0.39b	1.27b	16.68d	4.19c	2.17d	1.04f	0.03d	0.0b	0.10	0.04	0.11	0.05	0.0	0.04
A10	3.77c	2.07b	0.48a	1.26b	35.97a	7.14a	4.19b	3.25b	0.10b	0.0b	0.17	0.05	0.13	0.13	0.0	0.06
A20	4.61b	2.51a	0.51a	1.45a	33.42ab	5.31b	4.69b	2.21d	0.9bc	0.0b	0.10	0.04	0.11	0.09	0.0	0.05
A50	5.78a	2.37ab	0.38b	1.47a	31.24b	5.72b	5.79b	1.71e	0.08c	0.0b	0.04	0.03	0.11	0.05	0.0	0.04
National	nix	nix	nix	nix	nix	0.3	nix	0.05-5	0.05-1	0.05-1	nix	nix	nix	nix	nix	nix

Nix = no data, The bio-concentration factor for every heavy metal is computed through the ratio of heavy metal level in above-ground biomass of grass and soil. In a column, different lowercase letters show significant differences at ($p < 0.05$) between treatments

4. Discussion

The influences of corn stalk biochar treatment on physicochemical traits of rural soil Increasing information has exposed that the influences of biochar treatment on the soil physicochemical attributes rely on the kind of biochar, application amount, and soil. Generally, soil physicochemical traits prolong their alterations by enhancing the biochar applied rates (Murtaza *et al.* 2021a). The findings in this research supported this conclusion. Lignocellulosic materials derived from biochars such as wood and crop straws generally have higher than 40% C, lower ash content, and pH 6.46 to 11.00. Hence, biochar treatment can expressively increase SOC, particularly stable organic carbon (Duwiejuah *et al.* 2020; Mehmood *et al.* 2023). Conversely, biochar obtained from livestock and dairy manure as well as other animal wastes generally comprise low carbon, but higher mineral nutrients and ash. Thus, biochars were observed to be mainly useful for enhancing plants' mineral nutrition (Luo *et al.* 2011; Hossain *et al.* 2015; Sarfraz *et al.* 2019). The corn stalk-derived biochar herein had characteristics similar to those of livestock residue obtained biochars and expressively improved mineral nutrient levels of rural soil. The mulching impacts of biochar treatment generally noticed in acidic soils (Oni *et al.* 2021), were not clear in our work, partially due to lower alkalic constituents in applied biochar comprised, leading to low mulching impacts, and partially because of the alkaline the employed rural soil. Tian et al. (2021) observed a slight alteration in the pH range in the alkaline soil treated with silver grass biochar, in comparison with significant enhancement in the acidic soil.

A substantial concentration of heavy metal contents in corn stalks typically limits its addition as a soil improver. The pyrolysis process mainly decreases the heavy metals' bio-availability in corn stalks, whereas their amounts in the biochar were enhanced (Puga *et al.* 2015). It was logical that the heavy metal elements in biochar-treated soil proportionally enhanced with the biochar application rate. It should be observed that greater than 30 % of biochar application rate might cause too high heavy metals that even surpass the WHO and national allowable limits. In the present work, ameliorating corn stalk biochar caused slight variations of the fractions of Cd, Cr, Pb, and Cu in rural soil, though total amounts of heavy metals enhanced notably. Though, corn stalk biochar treatment considerably decreased the residual fractions of the Zn and As but increased the reducible, oxidizable, and acid-soluble fractions which might indicate that corn stalk biochar enhanced the bio-availability of Zn and As because reducible, oxidizable, and acid-soluble fractions were supposed to have higher bio-availability (Ran *et al.* 2016). Up to now, we have a not visible understanding of the processes by which biochar addition affects the fractions of soil heavy metals. There are 3 conceivable processes of biological transformation precipitation and adsorption. The inorganic constituents like oxides, carbonates, and phosphates in biochar can cause the precipitation of heavy metals, which may increase the comparative fractions of heavy metals in char-treated soil (Rasool *et al.* 2021). The different functional groups, for instance, hydroxyl, phenolic, and carboxyl on the surface of porous biochar can sorb the heavy metals by coordination, and chelation which is ascribed to enhance oxidizable acid-soluble heavy metals (Murtaza *et al.* 2021b). Further research is needed to understand the procedure by which biochar alterations the bio-available fractions of heavy metals and their ecological effects.

A large number of experiments have presented that the biochar treatment can expressively enhance the growth of plant and mineral nutrition, as well as finally enhance grain yield (Duwiejuah *et al.* 2020). We achieved similar findings in this research. Furthermore, no negative effects were noticed at a very higher degree of 50% in the mass ratio of the soil to the biochar, in comparison with the results in which immense biochar addition could suppress the growth of the plant and subsequently decrease the yield (Rizwan *et al.* 2016). Increasing information has revealed that biochar application can decrease the bio-availability of soil heavy metals and thus diminution their accumulation in the plant tissues (Tomczyk *et al.* 2020). For instance, corn stalk biochar suppressed the accumulations of Pb, Cr, Zn, As, Cu, Cd, and As in tomatoes (Zhang *et al.* 2007). Wang et al. (2021) too noticed that the biochar application expressively decreased the eatable tissue Pb and Cd contents and the total Pb and Cd uptake of the radishes and cabbages than the control samples. We got similar findings in this research. Altogether, mixing a sequence of corn stalk-derived biochar, varying from 1% - 50% in mass fraction, decreased the accumulations of the heavy metal contents in the grass above-ground biomass though total heavy metals contents enhanced very much in biochar-treated soils, which might show that corn stalk biochar, same with other biochars, played a role in decreasing activity of the soil heavy metals. Contrastingly, these findings might indicate that the total amount of heavy metal contents was not intimately linked with their bio-availability. Remarkably, the enhanced bio-available arsenic in soil did not enhance the accumulation of arsenic in grass above-ground biomass (Wang *et al.* 2016). Muhammad et al. (2017) stated that the little cadmium accumulation in the shoot of both ryegrass and corn but high cadmium accumulation in their roots resulted in biochar treatment. Xu et al. (2016) proposed that the creation of insoluble metal phosphates inside root tissues might suppress the metal's translocation from roots to shoots. More research is needed to understand the particular procedures.

5. Conclusions

Corn stalk biochar amendment induced improvement of poor rural soil fertility, grass nutrition, and plant growth as well. The accumulation of these heavy metals in grass aboveground biomass was reduced though the biochar-amended soils had much higher total heavy metals. The corn stalk biochar was likely to be a potential conditioner for rural soil.

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Conflict of Interest

"The authors declare no conflict of interest".

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