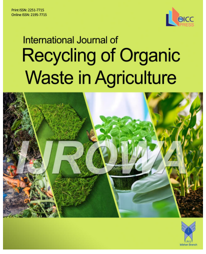

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Improvement of soil quality through biochar in rice under wastewater irrigated soil: Effects on heavy metals reduction

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Original Research

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Abstract:

Purpose: Rice, a global staple, can accumulate high levels of heavy metals especially Chromium (Cr) when grown in a soil irrigated with tannery effluent over time, potentially reaching toxic levels for human consumption. Biochar offers a cost-effective solution by binding these heavy metals in soil, reducing their bioavailability and mitigating health risks. The present study offers a two-way solution of reducing weed load of agricultural fields through parthenium biochar preparation and its application in Cr contaminated soil with aim of its lower accumulation in the edible part of the crop.

Method: The investigation consists of ten treatments in completely randomized design with three replications using simple and concentrated H_3PO_4 and 1 M $FeCl_3$ modified biochar at graded dose and one biochar untreated control. All treatments receive a recommended dose of NPK fertilizers.

Results: Our study shows that biochar produced from parthenium can reduce uptake of heavy metals in the plant body. Moreover, modification of biochar by H_3PO_4 and $FeCl_3$ hastened the metal fixation and further reduced the metals accumulation in different parts of plant body depicted by lowering translocation factor (TF) along with translocation coefficient (TC).

Conclusion: Overall, application of biochar is proven to reduce the metals accumulation in rice plant parts and grains rendering it a good amendment.

Keywords: Biochar; Contamination; Heavy metals; Rice; Translocation

1. Introduction

Soil sustains vital ecosystem services but faces ongoing threats from human activities (Zafar et al., 2021). Heavy metal contamination in farmland is often linked to human induced industrial activities, posing risks to crop quality and exerts a detrimental effect on human health (Kaur et al., 2018). Trace metals, spread over large areas through wind transfer, erosion, leaching, are persistent, non-biodegradable and lead to cancerous and genetic risks through bio-accumulation in living systems (Wahiduzzaman et al., 2021). Therefore, remediating heavy metal-contaminated soil is vital for environmental protection (Radziemska et al., 2017). Management of multi-metal-polluted soils such as arsenic (As), cadmium (Cd), lead (Pb), chromium (Cr), copper (Cu), zinc (Zn), etc. is challenging due to the diverse characteristics of these metals. Possible confinement approaches might involve sorption, precipitation, and complexation reactions, but they can also be taken up by plants, get leached as well as volatilized from the soil (Bolan et al., 2014). Besides this, plants employ various resistance mechanisms to combat heavy metal stress. These mechanisms include blocking of metal assimilation, extracellular and cytoplasmic complexation, chelation and moreover production of stress-inducible proteins (Yu et al., 2019). However, the primary detoxification method in plants involves sequestering heavy metals within vacuoles through complexation with small peptides, such as phytochelatins (Dubey et al., 2018).

The leather industry in Jajmau, Kanpur city, originating in colonial India, remains prosperous with numerous tanneries producing various leather goods. Effluent from the treatment plant severely contaminated soils, especially with Chromium (Cr), in nearby irrigated areas. Bhattacharya et al. (2019) found that soil samples near dump sites had Cr levels ranging from 0.1 to 0.56 g/kg, far exceeding the baseline Cr concentration of 0.12 mg/kg in uncontaminated soils, indicating significant soil contamination in this region. Elevated Cr levels in agricultural fields near Kanpur are due to irrigating fields with Cr contaminated groundwater and direct runoff from dump sites during monsoons. Paul et al. (2015) reported Cr concentrations of 40,500 mg/kg in soil containing tannery sludge in Kanpur, with 1,400 mg/kg as Cr(VI). About 65% of total Cr is prone to leaching under acidic conditions, highlighting the urgent need to address soil contamination in this area.

Soil amendments play a critical role for crop cultivation in metal-contaminated soils either by removal or by reducing their toxic effects on plants. Among them, biochar poses high sorption capacity due to its enormous surface area, exceptionally porous structure and numerous functional groups (Mu et al., 2019) which enable it to be a sustainable metal toxicity remediator. Additionally, micropores in biochar are responsible for sorbing dissolved organic matter and promoting microbiological activity (Zama et al., 2018) making it a powerful soil amendment. The type of metal ions influences the mechanisms governing their sorption by biochar, such as complexation, cation exchange, precipitation for Cd, Pb and Ni while electrostatic interactions, and reduction for Cr (Xu et al., 2016). However, a report on decreased nutrient availability and inhibition of plant growth by biochar application is a matter of concern (Beesley and Marmiroli, 2011) for its extensive use. The binding reactions between heavy metals and biochar surfaces are reversible, allowing desorption of adsorbed heavy metals (HMs) on long run (Melo et al., 2016). This reversible nature of biochar interactions is significant because it can affect the soil-to-plant transport of heavy metals, ultimately impacting crop quality and consumer health. As a recent strategy, modification of biochar through various agents like steam, acid or base solutions, neutral salt and even nanomaterials are done to enhance its effective surface area, pore volume and surface-active functional groups that helps in enhanced retention of metals both in terms of quantity and times (Liu et al., 2022).

Rice (*Oryza sativa* L.) is grown extensively throughout the world, serve as a staple food for south-Asian countries (Rizwan et al., 2016); also, frequently prone to heavy metal toxicity which reduces its growth and grain yield (Shraim, 2017), ultimately affecting food ecosystems dependent on rice, especially a large human community. In this respect, understanding the complex interactions between heavy metals, soil, plants and its transfer through food consumption is crucial for effective remediation of contaminated soils, protecting crop quality, and safeguarding human health. Our study highlights the extent of Cr contamination in rice food grains of the tannery effluent irrigated soil of Kanpur area, which is still relatively unexplored. Moreover, use of modified biochar application in these soils as a remediation strategy and its effect on distribution of heavy metals especially Cr in different parts of paddy plant is scarce in previous literature.

To address the aforementioned issues, it is hypothesized that biochar, especially the modified biochar, with its high capability for heavy metals sorption can effectively bind the heavy metals within soil and subsequently reduce its bio-accessibility. Thus, the primary objective of this study lies in the reduction of heavy metals in rice grain and exploring its distribution in different parts of paddy plant with the assumption of lowering metals transport from soil to plant in order to document ameliorating effect of modified biochar.

2. Materials and methods

Sampling of soil and conduction of pot experiment

Chromium contaminated soil is collected from Kanpur city, Uttar Pradesh, India in July, 2022 from farmers' fields (26º26′59.7″ N and 80º19′54.7″ E) which was irrigated by tannery effluent wastewater. For tanning purposes, basic chromic sulphate is used, which comes in the effluent of these industries. Though, before discharge these effluents are purified but substantial amount of toxic metal Cr remains in the effluent which when used in irrigation cause Cr accumulation in the soil. Several researchers (Sinha et al., 2006; Paul et al., 2015; Dotaniya et al., 2017) have reported presence of Cr in soils of Kanpur city and its surrounding areas till date. GPS based sampling was done with spade in $0-20$ cm soil depth in 'V' shape and the soil is transported to Net house of Department of Soil Science and Agricultural Chemistry, Banaras Hindu University, Varanasi (25º19′3.52″ N; Longitude, 82º58′26.09″ E), India. The soil is then air dried, ground and sieved with 2 mm sieve and filled up into the pot after thorough mixing with biochar as per application dose under varying treatments as outlined in Table 1.

The initial soil was mildly alkaline ($\text{pH} = 7.6$) loamy textured with high organic carbon (2.04%) containing 1.15, 0.2, 0.1 and 0.017 g/kg of total Cr, Pb, Ni and Cd, respectively; which is much higher than the permissible limit of $0.1-0.2$, $0.09-0.3$, $0.05-0.08$ and $0.002-0.003$ g/kg for Pb, Ni and Cd, respectively (Kabata-Pendias, 2011). Earthen pots were lined with thin sheet of plastic to check the water loss during this experiment. All treatments were replicated thrice in a completely randomized design. Irrigation with tap water was given to the pot as and when required to maintain submerged (5 cm standing water from the surface of the soil filled in the pot) condition. The recommended dose of N, P_2O_5, and K_2O for rice was administered at the rate of 120:60:60 kg/ha using urea, Di-ammonium phosphate (DAP), and potassium chloride (commonly known as muriate of potash or MOP), respectively, as source of

Table 1. Treatment details employed in the experiment.

Treatment code	Treatments details	Abbreviations used
T1	Control	C
T2	Simple biochar @ 5 t/ha	SBC_5
T3	Simple biochar @ 7.5 t/ha	$SBC_{7.5}$
T4	Simple biochar @ 10 t/ha	SBC_{10}
T5	H_3PO_4 modified biochar @ 5 t/ha	PBC_5
T6	H_3PO_4 modified biochar @ 7.5 t/ha	$PBC_{7.5}$
T7	H_3PO_4 modified biochar @ 10 t/ha	PBC_{10}
T8	$FeCl_3$ modified biochar @ 5 t/ha	FBC_5
T9	$FeCl_3$ modified biochar @ 7.5 t/ha	$FBC_{7.5}$
T10	$FeCl_3$ modified biochar @ 10 t/ha	FBC_{10}

*In all treatments recommended dose of fertilizers are applied @ 120:60:60:: N: P_2O_5 : K_2O (kg/ha).

N, P, and K. All-inclusive dose of P and K fertilizers were applied before transplanting, and N was applied in 2 splits; of which 50% as basal dose before transplanting and at 30 days after transplanting (DAT) after solubilization in distilled water. Eight seedlings of rice (var. HUR-105) were transplanted in each pot however; for appropriate nurturing, only five plants were retained till last after thinning, and the pots were perpetuated in weed free condition by manual weeding throughout the investigational period. Harvesting of seedings were done by sickle with stubbles remaining 5 cm from the soil surface to avoid unwanted contamination.

Climatic data during the experiment

The transplanting of Rice is done in the third week of July, 2022 and was harvested in the second week of November, 2022 with 108 days growing period. Meteorological data during this time reveals the mean maximum temperature was 30.2 °C observed in th third week of August. Maximum rainfall is obtained in the 4^{th} week of July. But distribution of rainfall due to southwestern monsoon rains is very uneven during this stipulated time period with mean average rainfall of 48.15 mm during the entire period (Dotaniya et al., 2017). Basically, it is a mild temperate rainy climate (C type) according to Köppen climatic classification. While average sunshine hours, evaporation and wind speed gradually decrease with advancement of crop growth peaking at 28^{th} week of the year.

Preparation of biochar

Biochar is prepared using methods outlined by Kumar et al. (2013), and modified by the methods outlined by Zheng and Duan (2022) for FBC ($FeCl_3$ modified biochar) and Wu et al. (2017) for PBC (H_3PO_4 modified biochar). Briefly, The *Parthenium hysterophorus* plant was collected, dried, chopped and passed through the 100-mesh sieve followed by pyrolyzed in a furnace at a temperature of 350 °C in N_2 environment for 45 min. Produced biochar from the pyrolysis was smoothly crumbled and sieved and mixed soil. For iron chloride modified biochar (FBC) and phosphoric acid modified biochar (PBC) modification methods were employed after pyrolysis.

Plant samples collection and analysis

In the laboratory analysis process, all three replications of plant samples were collected separately for root, stem and grain and the ultimate value presented is the mean of these three replicates. The plant samples were initially cleansed with a 0.2% detergent solution followed by dilute 0.1 M HCl solution and subsequently rinsed with double-distilled water. Following this, the samples were subjected to drying at a controlled temperature of 60 ± 5 °C for three days. Husks from the rice grains were separated. Subsequently, they were finely crushed and ground before undergoing digestion with a di-acid mixture composed of HNO_3 and $HClO_4$ in a 3:1 (v/v) ratio (Page et al., 1982). Finally, the samples were analyzed for Pb, Cd, Cr and Ni content utilizing an atomic absorption spectrophotometer, specifically the Agilent 240FS-AA model, manufactured by Agilent Technologies in Santa Clara, USA. The certified reference standards (CRS) for Pd (5190 – 8287), Cd (5190 – 8270), Cr (5190 – 8275), and Ni (5190 – 8298) were purchased from Agilent, USA. To ensure analytical preciseness, quality control samples were collected from substances with recognized attributes and adjusted to concentrations approximately the midpoint of their standardization range. The recovery rates for Pd, Cd, Cr, and Ni were 97.2, 98.5, 96.4 and 98.8%, respectively. The intermediate RSD values (%) for Pb, Cd, Cr and Ni were 0.40, 0.40, 0.87 and 0.93%, respectively.

Soil samples collection and analysis

Soil samples after rice harvest were collected when the soil became dry, mainly from the root rhizosphere regions. The dead roots were separated carefully and then the soil was finely grounded, passed through the 2 mm sieve before analysis. Tri-acid digestion was performed for total metal analysis of soil (Sparks et al., 1996).

Calculation of percentage of Cr reduction in different parts

The percentage of reduction of Cr affected by different biochar with varying dose is calculated on the basis of control treatment (T1) (Eid and Shaltout, 2016; Eid et al., 2017). For example, if X be the concentration of Cr in root of T1, and Y be the concentration of Cr in root of N^{th} treatment then percent reduction as per equation (1) will be:

$$\%\text{Reduction} = \frac{(X - YN)}{X} \times 100 \quad (1)$$

Translocation factor (TF) and translocation coefficient (TC) analysis

Translocation factor (equation (2)) and translocation coefficient (equation (3)) is calculated in compliance with the method outlined by Eid et al. (2017). He stated that if $\mathrm{TF} < 1$, then plants under metal stress and if $\mathrm{TF} > 1$, Hyperaccumulator plants.

$$\mathrm{TF} = \frac{S_c}{R_c} \tag{2}$$

where, S_c = Concentration of element in stem (µg/g), R_c = Concentration of element in root (µg/g).

$$\mathrm{TC} = \frac{P_c}{C_s} \tag{3}$$

where, P_c = Concentration of element in plants (µg/g), C_s = Content of element in initial soil (mg/kg).

Statistical analysis

In our experiment, a completely randomized design (CRD) was utilized, and all experiments were conducted in triplicate. The delineated values stand for the mean ± standard error (S.E.) derived from three separate and independent observations. To assess the statistical significance of the data, a One-way Analysis of Variance (ANOVA) was conducted using IBM SPSS 20.0, followed by Duncan's multiple range test (DMRT). Statistical significance was accustomed at a significance level of $P \leq 0.05$, enabling the evaluation of noteworthy distinctions among the mean values, following the methodology outlined by Gomez and Gomez (1984).

3. Results and discussion

Effect of biochar application on distribution of heavy metals in rice plant parts

Tannery effluent soil is mainly Cr contaminated as Cr is used in the tanning process as basic chrome sulphate. In our study, it is evident that initial soil contains the highest amount of Cr. It is over ten times than the WHO maximum permissible limits of 100 mg/kg. Although, Pb, Cd and Ni content in soil were also higher than the WHO permissible limits of 100, 3 and 50 mg/kg. Biochar application has remarkably diminished the heavy metals accumulation in different parts of rice. Maximum Pb, Cd, Cr and Ni accumulation was in rice roots irrespective of all the treatments (Table 2). Rice under the control treatment (C) showed a maximum of 11.4, 3.55, 302 and 18.8 µg/g of Pb, Cd, Cr and Ni respectively in roots. Roots are the primary part of

Table 2. Distribution of heavy metals (µg/g) in different plant parts of rice affected by biochar treatments
(Treatment means with different letters show significantly difference between them ($p \leq 0.05$) through DMRT).

Cr					Cd				
Treatments	Root	Stem	Husk	Grain	Treatments	Root	Stem	Husk	Grain
T1	387 ± 4.9^{a}	112 ± 4.0^{a}	48.9 ± 0.67^{a}	7.51 ± 0.10^{a}	T1	4.85 ± 0.14^{a}	1.34 ± 0.04^{a}	0.83 ± 0.02^{a}	0.63 ± 0.02^{a}
T2	367 ± 6.5^{b}	106 ± 3.4^{ab}	41.3 ± 0.57^{b}	7.06 ± 0.26^{ab}	T2	4.40 ± 0.06^{b}	1.26 ± 0.02^{b}	0.76 ± 0.02^{b}	0.53 ± 0.03^{b}
T3	349 ± 5.4^{c}	97 ± 1.1^{bcd}	35.9 ± 0.20^{c}	6.04 ± 0.16^{de}	T3	4.30 ± 0.04^{bc}	1.19 ± 0.01^{bc}	0.71 ± 0.01^{bc}	0.50 ± 0.02^{bc}
T4	328 ± 4.9^{de}	90 ± 2.3^{de}	32.8 ± 0.51^{cd}	5.60 ± 0.09^{ef}	T4	3.89 ± 0.10^{de}	1.11 ± 0.03^{d}	0.67 ± 0.01^{cd}	0.47 ± 0.01^{cd}
T5	341 ± 5.3^{cd}	95 ± 4.5^{cde}	33.8 ± 0.90^{cd}	6.49 ± 0.14^{cd}	T5	4.19 ± 0.07^{bc}	1.21 ± 0.02^{b}	0.72 ± 0.01^{bc}	0.49 ± 0.01^{bc}
T6	318 ± 5.8^{ef}	86 ± 1.5^{ef}	27.9 ± 0.18^{de}	4.96 ± 0.18^{g}	T6	3.89 ± 0.08^{de}	1.09 ± 0.02^{d}	0.68 ± 0.01^{cd}	0.45 ± 0.02^{cd}
T7	292 ± 7.0^{g}	74 ± 3.1^{g}	24.8 ± 0.46^{e}	4.07 ± 0.20^{h}	T7	3.78 ± 0.08^{ef}	1.06 ± 0.02^{d}	0.63 ± 0.01^{de}	0.42 ± 0.01^{d}
T8	345 ± 8.5^{cd}	101 ± 4.3^{bc}	34.0 ± 0.57^{cd}	6.69 ± 0.12^{bc}	T8	4.10 ± 0.11^{cd}	1.22 ± 0.03^{b}	0.63 ± 0.02^{de}	0.48 ± 0.02^{bcd}
T9	327 ± 4.9^{de}	91 ± 1.5^{de}	29.3 ± 0.23^{cde}	$5.22 \pm 0.13\text{f}^{g}$	T9	3.72 ± 0.10^{ef}	1.13 ± 0.02^{bc}	0.59 ± 0.01^{e}	0.44 ± 0.02^{cd}
T10	302 ± 5.7^{fg}	79 ± 4.2^{fg}	25.7 ± 0.95^{e}	4.11 ± 0.12^{h}	T10	3.55 ± 0.07^{f}	1.11 ± 0.02^{d}	0.58 ± 0.02^{e}	0.43 ± 0.02^{d}
SEm ±	6.27	3.39	2.08	0.16	SEm ±	0.09	0.02	0.02	0.02
CD	18.8	10.1	6.24	0.49	CD	0.26	0.07	0.05	0.06
($p \leq 0.05$)					($p \leq 0.05$)				

Pb					Ni				
Treatments	Root	Stem	Husk	Grain	Treatments	Root	Stem	Husk	Grain
T1	15.6 ± 0.52^{a}	3.67 ± 0.10^{a}	1.41 ± 0.02^{a}	0.57 ± 0.02^{a}	T1	23.6 ± 0.47^{a}	10.0 ± 0.31^{a}	5.49 ± 0.22^{a}	3.10 ± 0.23^{ab}
T2	14.8 ± 0.32^{a}	2.74 ± 0.08^{b}	1.06 ± 0.02^{b}	0.43 ± 0.01^{b}	T2	22.8 ± 0.26^{ab}	9.64 ± 0.33^{ab}	5.23 ± 0.10^{ab}	2.55 ± 0.12^{ab}
T3	14.1 ± 0.21^{bc}	2.56 ± 0.04^{c}	0.98 ± 0.03^{c}	0.40 ± 0.01^{c}	T3	21.9 ± 0.40^{b}	9.33 ± 0.14^{abc}	5.09 ± 0.25^{ab}	2.25 ± 0.13^{abc}
T4	14.0 ± 0.18^{bc}	2.47 ± 0.03^{c}	0.96 ± 0.02^{c}	0.39 ± 0.01^{c}	T4	19.8 ± 0.42^{cde}	8.47 ± 0.40^{de}	4.85 ± 0.20^{bcd}	2.05 ± 0.10^{bc}
T5	14.2 ± 0.23^{bc}	2.46 ± 0.02^{c}	0.95 ± 0.02^{c}	0.38 ± 0.00^{c}	T5	20.2 ± 0.55^{cd}	8.63 ± 0.24^{cd}	4.92 ± 0.14^{bc}	2.35 ± 0.12^{abc}
T6	13.4 ± 0.27^{cd}	2.24 ± 0.04^{d}	0.87 ± 0.02^{d}	0.35 ± 0.01^{d}	T6	19.1 ± 0.36^{cde}	8.31 ± 0.17^{de}	4.71 ± 0.16^{bcd}	1.92 ± 0.08^{bcd}
T7	11.5 ± 0.47^{f}	2.02 ± 0.05^{e}	0.79 ± 0.02^{e}	0.32 ± 0.01^{e}	T7	18.7 ± 0.35^{e}	7.88 ± 0.23^{e}	4.34 ± 0.16^{d}	1.54 ± 0.16^{d}
T8	13.5 ± 0.38^{bc}	2.44 ± 0.03^{c}	0.95 ± 0.02^{c}	0.38 ± 0.01^{c}	T8	20.4 ± 0.55^{c}	8.89 ± 0.25^{bcd}	4.97 ± 0.17^{abc}	2.13 ± 0.04^{a}
T9	12.3 ± 0.63^{de}	2.17 ± 0.03^{de}	0.83 ± 0.02^{de}	0.33 ± 0.01^{de}	T9	19.8 ± 0.52^{cde}	8.61 ± 0.23^{cde}	4.70 ± 0.10^{bcd}	1.84 ± 0.05^{abc}
T10	11.4 ± 0.33^{f}	1.85 ± 0.04^{f}	0.72 ± 0.02^{f}	0.26 ± 0.01^{f}	T10	18.8 ± 0.46^{de}	8.18 ± 0.21^{de}	4.52 ± 0.13^{cd}	1.61 ± 0.13^{cd}
SEm ±	0.39	0.05	0.02	0.01	SEm ±	0.46	0.27	0.17	0.13
CD	1.17	0.15	0.06	0.03	CD	1.38	0.81	0.52	0.37
($p \leq 0.05$)					($p \leq 0.05$)				

a plant which is exposed to soil for fetching nutrients. So, obviously roots encounter the primary stress due to heavy metals in soil. As a plant defense mechanism, it binds metals within its structure using different chelating agents, transfer it to vacuoles and subsequently reduces its transfer to other parts of the plant body. Eid and Shaltout (2016) stated that the substantial buildup of heavy metals within plant roots occurs owing to the binding of these metals with sulfhydryl groups, which restricts their translocation to the above-ground parts. With increasing doses of biochar, metal accumulation has significantly reduced. A 10 t/ha application rate of simple biochar (SBC) has reduced the Pb, Cd, Cr and Ni content of root by 10.3, 19.8, 15.2 and 16.1%, respectively. But employment of PBC and FBC has further reduced it as compared to SBC. The PBC at 10 t/ha has declined the Cr alone by 24.5% while FBC by 22%. The Pb and Cd content in root was lowest under T10 receiving FBC @ 10 t/ha. Although T7 had statistically similar results to T10. Latare et al. (2018) noted that the aerial parts of plants exhibited low levels of lead accumulation, with the majority of lead being stored in the root system.

The maximum reduction of all heavy metals content in the stem part obtained in T7 was 1.5, 1.3, 1.8 and 1.3 times, respectively for Cr, Cd, Pb and Ni over the control treatment. However, T3, T4, T5 and T9 showed no statistical dissimilarity in terms of reducing Cr concentration in the stem. Husks of rice grain also showed considerable amount of metals accumulation. The control treatment showed 48.9, 5.49, 1.41 and 0.83 µg/g of Cr, Ni, Pb and Cd accumulation in grain husk of rice, respectively. The maximum reduction of Cr and Ni in husk was obtained under T7, while the maximum reduction of Pb and Cd was in T10. When biochar was applied, it influenced the soil environment by modulating physiochemical and biological properties. In our study, application of biochar had significantly reduced the metals accumulation in root by fixing them in soil only and reducing its bioavailability. This observation was similar to the findings of Mu et al. (2019) and can be clarified by the fact that Pb, Cr, Ni and Cd in the amended soils are rendered immobile, consequently preventing the metals being transported from the soil to the plant roots. In most of the cases T4 showed statistically at par results with T5, T6, T8 and T9. This depicted that, application of 5 or 7.5 t/ha of modified biochar had similar results with that of 10 t/ha simple biochar application. Biochar has a high specific surface area and surface-active functional groups through which they can fix heavy metals in their structure. Modification of biochar with H_3PO_4 leads to destruction of the biochar matrix and further enhances its surface area and also creates redox active functional groups in their surface. Similarly, Fe-modified biochar also destructs the pore structure. So, the metal binding ability of biochar is ultimately enhanced by modification procedure which is evident in our study.

Grain of rice, the main economic part of the plant, also accumulates heavy metals in considerable amounts. Content of lead in rice grains remains below the permissible limit of WHO/FAO i.e., 5 µg/g across all the treatments. But employment of biochar had further reduced it. Singh and Agrawal (2010) noted that a greater quantity of heavy metals in soil decreased crop yields by suppressing the activity of plant growth hormones like auxin and gibberellin. It also led to altered photosynthesis and transpiration efficacy, impeded photochemical light quenching, increased lipid and protein peroxidation, and elevated proline accumulation. Moreover, rice grown under submerged conditions alters redox potential of soil especially in rhizospheric zones. There is 50.3% reduction of Ni in rice grains obtained under T7 treatment compared to control (T1). Nickel is considered as an essential micronutrient in the plant body at low concentrations but it creates toxicity when accumulated at higher concentration. Aziz et al. (2015) reported that elevated nickel concentration (40 mg/kg) resulted in a notable reduction in both stem and root dry weights, chlorophyll level, rate of photosynthesis and transpiration, as well as stomatal conductance in rice. The Cr content of rice grains was above the safe limit of 5 µg/g in all treatments except T6, T7 and T10. A reduction of 34, 45.8 and 45.3% of Cr concentration was noticed under T6, T7 and T10 respectively over the control treatment. Raskin et al. (1997) unveiled that most metallic elements tend to be insoluble when inside plant vascular systems, resulting in their immobility within both extracellular (apoplastic) and intracellular (symplastic) compartments. These elements commonly precipitate in forms such as sulphates, phosphates, or carbonates. Moreover, the movement of metallic ions through the apoplastic pathway is hindered by the significant cation exchange capacity (CEC) found within cell walls, until the ion is carried away in a non-cationic metal chelate form.

Among the heavy metals, Cd, Pb and Ni remain as $+2$ cationic forms and these elements are redox inactive. They pose their toxicity by replacing the essential metallic counterpart of various enzymes, proteins, transporters and hormones. But Cr can remain in $+2$, $+3$ and $+6$ form even in the plant body, rendering it as a redox-active element. So, besides replacement of other elements from their biomolecular counterparts, Cr creates oxidative stress in the plant body. It can easily break down the hydrogen peroxide (H_2O_2) produced within the plant body and forms superoxide radicals and singlet oxygen species. Shahid et al. (2014) described that redox-active metals like chromium catalyze reactions such as the Haber–Weiss and Fenton reactions, generating hydroxyl radicals (OH•) when breaking down H_2O_2 at neutral pH. Conversely, metals like Pb, Cd, and Ni, which are not involved in redox reactions create covalent bonds with protein sulfhydryl groups (–SH) due to their electron-sharing tendencies, inhibiting enzymatic functions. Furthermore, heavy metals displacing essential cations from enzyme binding sites disrupted the balance of reactive oxygen species (ROS) within cells, leading to an excessive production of ROS. So, soil irrigated with tannery sludge containing higher quantities of Cr pose a great problem in crop cultivation. Employment of increasing dose of biochar had significantly reduced the Cr content of grains over the control treatment. Despite this, Cd content of grain had not been reduced to a safe limit of 0.3 µg/g even after application of 10 t/ha PBC and FBC. However, 46.5 and 33.3% reduction of Cd concentration in grain was noted in T7 and T10, respectively containing 10 t/ha of PBC and FBC. As regards to Cd concentration in grain, T4 showed statistically at par results with T6 and T8. This means, only 7.5 t/ha of modified biochar application was enough to reduce the Cd in grain similar to application of SBC @ 10 t/ha. Biochar modified with H_3PO_4 might immobilize heavy metals by forming their phosphate species. Mandal et al. (2017) found that alterations in the FTIR spectra of iron-modified biochar, both before and after the reaction with Cr(VI), indicated that the surface functional groups on the biochar, including carboxyl and carbonyl groups, played a role in reducing Cr(VI) to Cr(III) and adsorbing Cr(III) species on the biochar surfaces. Thus, modified biochar poses a great deal of metal fixing capability than the simple biochar, ultimately reducing Cr transfer from soil to plant and reducing its accumulation in rice grains.

Effect of biochar application on TF and TC of heavy metals in rice

Translocation factors of all heavy metals (Table 3) reduced to a great extent after application of biochar. For Cr, TF reduced by 3.5% in T2 over control despite being statistically similar to it. The maximum TF reduction of 1.2 times over control occurred in T7 followed by T10. After accumulation in the root, metals are gradually transported to other parts of the plant body. There are several mechanisms of heavy metals transport within plant body. Chen et al. (2014) outlined that in conditions of heavy metal stress, elevated H^{+}-ATPase activity restricts the transport of pollutant ions, potentially by enhancing the uptake of essential minerals, as there is competition for membrane transporters.

The sequence of TF of Cr in different treatments follows T1 > T2 > T8 > T3 > T5 > T4 > T8 > T6 > T10 > T7. Chromium is transported via sulphate carriers in plant bodies resembling Sulphur transportation. Shewry and Peterson (1974) explored that chromate absorption is also hindered by group VI anions like SO_4^{2-}, while the presence of Ca^{2+} supports its movement. This is because of the chemical resemblance to SO_4^{2-}, resulting in a mutual inhibition that affects the distribution of chromate. Conversely, calcium enhances the mobility of Cr(VI), playing a crucial role in the absorption and subsequent transport of metallic components in plants (Montes-Holguin et al., 2006).

Nickel translocation did not change significantly after application of graded dose of biochars in our experiment. Though there is a 6.5% reduction of TF for Ni in T7 compared to control treatment. Lead TF in rice plants also declined after application of graded dose of biochars. The maximum diminution of 1.5 times was recorded in T10 over control. Rest all the treatments showed no significant decline in TF for Pb. Mu et al. (2019) proposed that the effect of biochar resulted in an increased phytostabilization of Cd, Pb, and Cr within the roots, as evidenced by the examination of BCF values enhancing vetiver growth. Furthermore, they noted that the fixation of Cd and Pb in soils under biochar treatment had been associated with an increase in soil pH. In spite of this, translocation factor for Cd showed an increment in T10 and T9 treatments more than all other treatments in our study. All treatments showed at par results except T3 and T7 where significant reduction was observed over the control. Cadmium resembles mainly calcium transports. (Huang et al., 2017) dictated that the chemical resemblance between Ca and Cd implies that Ca can potentially mediate the physiological and metabolic responses induced by Cd in plants. Current research studies indicate that Ca can serve as an external agent to mitigate the detrimental effects of Cd stress on plants like growth inhibition, metal transport regulation, oxidative damage, photosynthesis reduction, and controlling signal transduction processes. If the TF and bioconcentration factor (BCF) values for a specific metal in a particular plant exceed 1, it signifies that the plant is a viable candidate for phytoextraction of that metal. Conversely, when TF is below 1, the plant is better suited for phytostabilization (Galal and Shehata, 2015).

Swain et al. (2021) concluded that plants do not uptake all

Table 3. Translocation factor of heavy metals in rice affected by biochar treatments
(Treatment means with different letters show significantly difference between them ($p \leq 0.05$) through DMRT)

Treatments	Pb	Cd	Cr	Ni
T1	0.363 ± 0.009^{a}	0.575 ± 0.009^{ab}	0.434 ± 0.005^{a}	0.788 ± 0.014
T2	0.287 ± 0.013^{b}	0.579 ± 0.013^{ab}	0.419 ± 0.001^{ab}	0.761 ± 0.012
T3	0.279 ± 0.009^{bc}	0.558 ± 0.009^{b}	0.398 ± 0.003^{cd}	0.762 ± 0.012
T4	0.273 ± 0.003^{bc}	0.577 ± 0.003^{ab}	0.391 ± 0.008^{de}	0.776 ± 0.025
T5	0.267 ± 0.005^{bc}	0.579 ± 0.005^{ab}	0.395 ± 0.004^{cd}	0.796 ± 0.009
T6	0.258 ± 0.003^{bc}	0.571 ± 0.003^{ab}	0.374 ± 0.002^{ef}	0.782 ± 0.011
T7	0.273 ± 0.012^{bc}	0.560 ± 0.012^{b}	0.353 ± 0.008^{g}	0.737 ± 0.028
T8	0.278 ± 0.011^{bc}	0.567 ± 0.011^{ab}	0.413 ± 0.005^{bc}	0.782 ± 0.003
T9	0.271 ± 0.014^{bc}	0.580 ± 0.014^{ab}	0.383 ± 0.002^{de}	0.765 ± 0.006
T10	0.250 ± 0.008^{c}	0.599 ± 0.008^{a}	0.361 ± 0.011^{fg}	0.760 ± 0.007
SEm ±	0.010	0.007	0.017	0.015
CD ($p \leq 0.05$)	0.029	0.022	0.006	NS

types of heavy metals from the soil in uniform amount, and this process is not solely influenced by metal concentration. Though TF has not reduced significantly for Ni in plant among all the treatments, TC for Ni from soil to plant has been noted to decline significantly after incorporation of graded dose of simple and modified biochars (Table 4).

The maximum reduction of 23.2% followed by 21.6% was in T7 and T10, respectively. The treatments T4, T5, T6, T8 and T9 showed more or less statistically at par results in reducing TC of Ni from soil to plant in our experiment. Lead and Cd also revealed similar types of results in reduction of TC. There was a 31.1 and 33% reduction of TC of Pb has been noted in our experiment in T7 and T10, respectively. In T10 there was 25.7% reduction of TC for Cd over control in our study. The T3, T5 and T8 were statistically at par in reducing TC of Cd in rice. Banerjee et al. (2016) found that the TF corresponding to Cr in vetiver growing in mined soil was 0.83. Meeinkuirt et al. (2013) found a TF measurement for Pb below one in vetiver growing in Pb mining waste, and Ghosh et al. (2015) found TF figures for As alongside Cd in vetiver cultivated in fly ash-administered sites to be beyond detectable levels.

The TC of Cr was also diminished in our study under graded dose of biochar application. Treatments T3, T5 and T8 showed no significant differences in TC describing that application of only 5 t/ha PBC and FBC was enough to mitigate Cr transfer to root from soil compared to application of 7.5 t/ha of SBC. Similarly, T4, T6 and T9 showed statistical similarity. However, the maximum of 1.4 followed by 1.34 times reduction of TC was obtained in T7 and T10 respectively with respect to control treatment. As per the findings of Skeffington et al. (1976), the transport of Cr(VI) is predominantly regulated by a sulphate carrier, while the uptake of Cr(III) by plants is primarily a passive process, characterized by its relatively low affinity. Lim et al. (2013) suggested that the key mechanism might involve metal precipitation by biochar mainly influenced by pH changes and their absorption onto the surface of the amendment. In this respect, modified biochars were more promising due to their higher capacity of metal fixation. Kharbech et al. (2020) documented that H^+-ATPase activity also plays a role in facilitating the sequestration of metals, thus mitigating the adverse effects of heavy metal toxicity.

Effect of biochar on reduction of Cr concentration in different parts of rice

We noted that plants took up more Cr than any other metals in our study as the content of Cr was more than the other metals concerned. So, the percentage reduction of Cr in different parts of rice compared to control after addition of different doses of biochar and modified biochar assumes importance (Fig. 1). There was a gradually increasing trend of Cr removal from different parts of rice with increasing dose of biochar. In T7, the maximum reduction of root Cr percentage was noted. Biochar positively impacted plant growth. Thus, it can modulate to some extent the translocation of heavy metals from one part of a plant to other part but this is still posing a further researchable issue as so many physiological factors are involved in this. Ahmad et al. (2017) documented that the accretion of heavy metals in plants is a complex process influenced by various factors, including soil properties, plant species, biochemistry in the root zone, and the competition for heavy metals uptake sites in plant roots. In terms of reduction of Cr in grain, where simple biochar had reduced only 6.1%, PBC @ 10 t/ha reduced it by 45.8%. The performance of FBC was comparable to PBC in reducing Cr in all parts of rice like grain, husk, stem and root. Ahmad et al. (2014) reported that phosphate present in biochar was found to immobilize Pb within soils through the creation of Pb-phosphate compounds. Moreover, in Fe-modified biochar Fe is also present with the surface functional groups which acts as a redox-active element. This can fix heavy metals by changing their oxidation states.

Table 4. Translocation coefficient of heavy metals in rice affected by biochar treatments
(Treatment means with different letters show significantly difference between them ($p \leq 0.05$) through DMRT)

Treatments	Pb	Cd	Cr	Ni
T1	0.106 ± 0.003^{a}	0.478 ± 0.013^{a}	0.481 ± 0.007^{a}	0.422 ± 0.008^{a}
T2	0.095 ± 0.002^{b}	0.435 ± 0.008^{b}	0.452 ± 0.008^{b}	0.403 ± 0.007^{ab}
T3	0.090 ± 0.001^{bc}	0.418 ± 0.004^{bc}	0.423 ± 0.007^{c}	0.386 ± 0.006^{b}
T4	0.089 ± 0.001^{bc}	0.384 ± 0.009^{de}	0.395 ± 0.007^{de}	0.352 ± 0.008^{cd}
T5	0.090 ± 0.001^{bc}	0.413 ± 0.006^{bc}	0.412 ± 0.006^{cd}	0.362 ± 0.008^{c}
T6	0.084 ± 0.002^{c}	0.382 ± 0.005^{de}	0.378 ± 0.007^{ef}	0.341 ± 0.005^{cde}
T7	0.073 ± 0.003^{de}	0.368 ± 0.005^{ef}	0.342 ± 0.009^{g}	0.324 ± 0.005^{e}
T8	0.087 ± 0.002^{c}	0.402 ± 0.011^{cd}	0.422 ± 0.010^{c}	0.364 ± 0.010^{c}
T9	0.078 ± 0.003^{d}	0.367 ± 0.008^{ef}	0.392 ± 0.006^{de}	0.350 ± 0.009^{cd}
T10	0.071 ± 0.002^{e}	0.355 ± 0.004^{f}	0.357 ± 0.008^{fg}	0.331 ± 0.009^{de}
SEm ±	0.002	0.008	0.008	0.008
CD ($p \leq 0.05$)	0.006	0.024	0.024	0.023

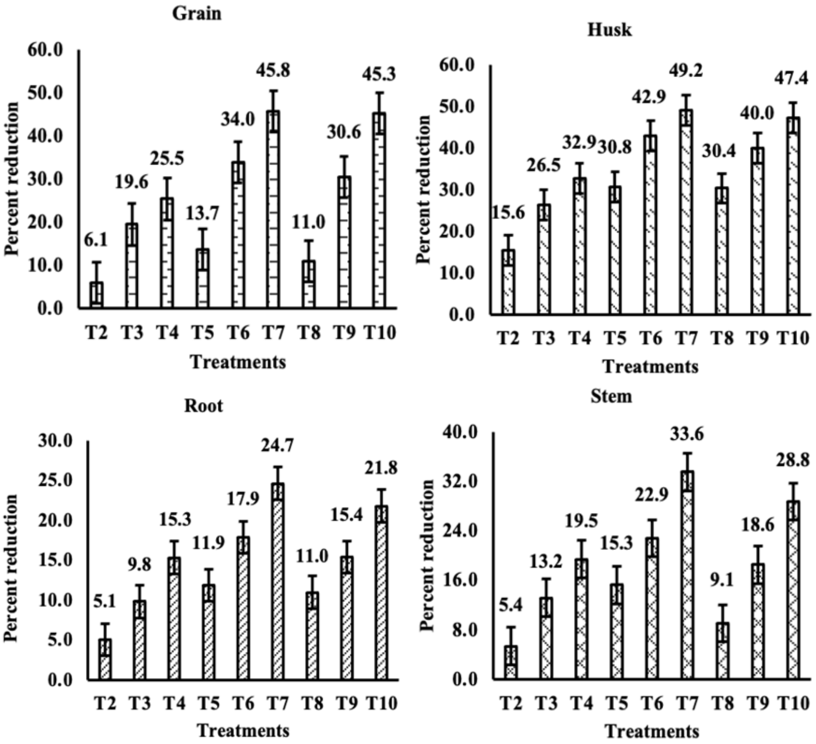

Figure 1. Percentage reduction of Cr concentration in different parts of rice over control treatment under different treatments after application of graded dose of biochar
(Data represents mean ± SE of three independent replication and error bars identify standard errors of different treatments).

Total metals concentration in soil

Total concentration of Cd, Ni, Cr and Pb in post-harvest soils showed no significant differences among different treatments (Fig. 2). Total Ni concentration in post-harvest soil varies from 99.1 to 99.8 mg/kg, while total Cd, Cr and Pb from 15.1 to 15.9, 1151 to 1154 and 198.1 to 199.2

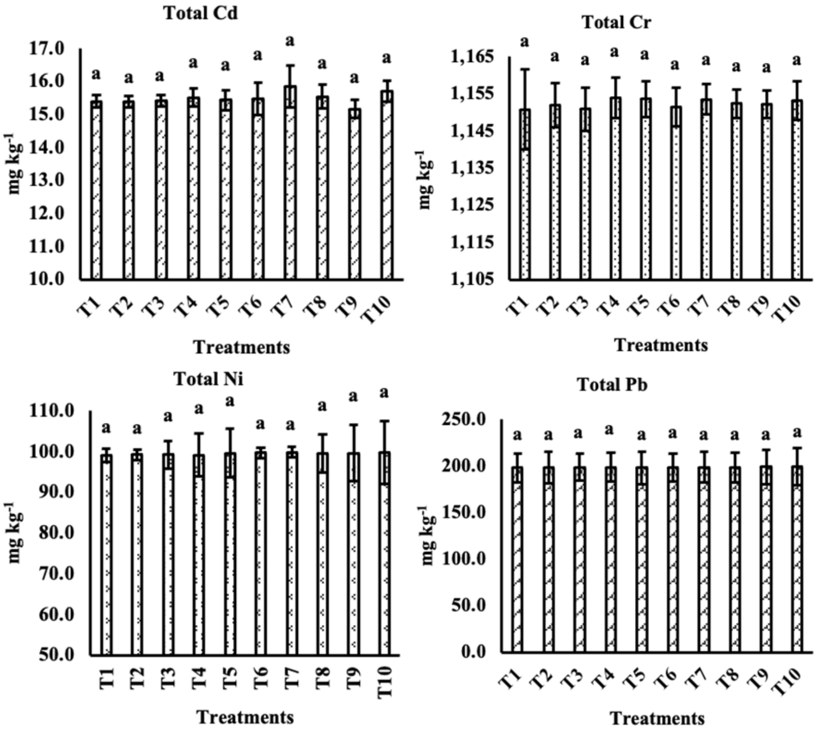

Figure 2. Total content of heavy metals in post-harvest soil
(Data represents mean ± SE of three independent replication and treatment means with different letters show significantly difference between them ($p \leq 0.05$) through DMRT. Error bars identify standard errors of different treatments).

mg/kg. But biochar administration cannot reduce the total metal content of the soil as after mixing of biochar with soil we cannot remove it except some type of magnetic biochar which could be removed from soil using magnets. Lu et al. (2018) observed that the use of biochar led to higher levels of residual Zn and Pb. The elevated levels of Pb in the phosphorus-rich biochar treatments were possibly a result of Pb-P bonding. In a separate investigation, Jiang et al. (2012) noted an augmentation in the residual Cu after the addition of biochar. Similarly, transfer of HMs from soil to plant also diminished.

4. Conclusion

Our study revealed that simple and modified biochar reduced the concentration of Cd, Ni, Cr and Pb in different parts of rice. Application of PBC at 10 t/ha had declined the root concentration of Cr to a tune of 24.5%, while grain concentration was reduced by 45.8% over the control treatment. Similarly, FBC also reduced uptake of Cd, Ni, Cr and Pb in different plant parts. Performance of modified biochar at lower rates produced statistically similar results with that of higher dose of simple biochar depicting its higher effectiveness. Reduction of TC and TF within plant emphasized the beneficial effect of biochar application to rice.

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Authors contributions
Conceptualization: SM and SKS; Soil sampling and analysis: SM and SSJ; Data analysis: AP and SSJ; Writing-original draft preparation: SM, SKS and AP; writing-review & editing: RJB, SKS and SSJ. All authors have read and agreed to the published version of the manuscript.

Availability of data and materials
The data that support the findings of this study are available from the corresponding author, upon reasonable request.

Conflict of interests
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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