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Adsorption and Distribution Pattern of Zinc in Soils Amended with Different Types of Biochars

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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Original Research Article

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Abstract

Greenhouse and laboratory experiments were conducted to study the adsorption and distribution pattern of zinc in soils amended with different types of biochars. Representative red and black soil samples were collected from plot numbers 125 and 162, respectively, at the Main Agricultural Research Station, Raichur. Maize cob rind, pigeonpea stalk and cotton stalk biochars were applied separately to both soils at 10, 15 and 20 t ha-^{1}. The soil-biochar mixtures were incubated for up to 120 days at near field-capacity moisture and used for experimentation. The results showed that biochar application at different rates increased soil pH, organic carbon, cation exchange capacity (CEC), water-holding capacity and available major and secondary nutrients, while decreasing bulk density in both soil types. The zinc adsorption data fitted the Freundlich adsorption equation better than the Langmuir equation. Freundlich distribution coefficient (KD) values were higher in black soil treatments than in red soil treatments; therefore, the sorption capacity for zinc was comparatively higher in black soil than in red soil amended with different biochars. Among the biochars, zinc adsorption decreased in the order cotton stalk > pigeonpea stalk > maize cob rind, irrespective of soil type.

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Furthermore, zinc distribution coefficients were strongly correlated with pH, EC, OC, cation exchange capacity and bulk density. Native zinc was preferentially distributed in the order RES-Zn > CAB-Zn > ORG-Zn > EXC-Zn, whereas adsorbed zinc at the higher addition level (200 µM L^{-1}) showed a marginal shift compared with the original partitioning of native zinc and followed the sequence CAB-Zn > RES-Zn > ORG-Zn > EXC-Zn.

Keywords: Soil; biochar; zinc; adsorption isotherm; distribution coefficient; distribution fractions.

1. Introduction

In recent years, there has been increased interest in understanding the chemistry of zinc in soils in relation to contamination and environmental accumulation, as zinc is an essential micronutrient that performs various physiological functions in living systems. The indiscriminate use of industrial waste amendments in agriculture for recycling may contribute to this concern. The absence of systematic protocols and established monitoring norms may further aggravate the consequences. These effects depend on soil type, the quality and quantity of amendments, and their influence on soil properties. The concentration of zinc in soil solution at a given time often provides a useful measure of soil quality or contamination because it is directly related to mobility and plant uptake. Soil solution concentration, and therefore bioavailability and toxicity, is likely controlled by retention and release reactions between zinc and the soil matrix. Zinc retention by the solid phases of soil is governed by several mechanisms, including adsorption to surface-active minerals and humic constituents through ion exchange and specific adsorption, diffusion into primary and secondary mineral structures, and precipitation.

In general, specific sorption of zinc by soil colloids and its subsequent desorption are the main mechanisms controlling the retention or release of zinc in soils (Tiller et al., 1984). The extent of sorption-desorption varies among soils because it is influenced by several soil properties. Zinc sorption is known to be strongly pH dependent (Harter, 1983; Bar-Tal et al., 1988; Stahl and James, 1991; Dang et al., 1994). Soil pH influences not only the amount of zinc sorbed but also the shape of the sorption isotherm (Harter, 1983; Msaky and Calvet, 1990).

Zinc availability to plants is associated with the distribution of this nutrient among soil fractions. Therefore, understanding zinc distribution among soil fractions helps to characterise its soil chemistry and potential availability for plant uptake. However, the distribution of zinc among chemical forms may vary significantly in response to changes in soil properties. Although crops require zinc only in small quantities, it is indispensable nutritionally, and deficiency can lead to several plant disorders because zinc is associated with several enzymes. Parent material, pedochemical transformations and anthropogenic interventions contribute to zinc distribution and bioavailability for plant uptake. For effective and efficient resource management, a clear understanding of zinc fractions is essential.

Recent evidence also indicates that biomass-derived biochar can affect the adsorption and desorption of metals, including Zn, through changes in sorption surfaces and soil chemical conditions (Das, 2024; Wei et al., 2025).

1.1 Biochar as an Amendment

As an emerging carbonaceous material, biochar has been extensively studied as an amendment for soil remediation. Several studies have reported the immobilisation behaviour of Zn on biochars derived from different biomass sources, and some have proposed immobilisation mechanisms that indicate an important role of biochar ash in Zn immobilisation. Because biochars generally have higher surface area and greater cation exchange capacity (CEC) than native soil constituents, they have been tested to reduce the solubility and toxicity of Zn, particularly in heavy metal-contaminated soils or industrial waste disposal sites. However, higher biochar application rates in normal agricultural soils may affect Zn bioavailability by changing soil properties, increasing sorption and decreasing desorption, which may adversely influence crop growth and development.

Biochar production and activation methods are relevant because feedstock and pyrolysis conditions influence carbon content, surface area, cation exchange capacity and nutrient-retention behaviour (Bambhaniya & Gojiya, 2025).

Recent field evidence also shows that biochar-based amendments can reduce bulk density and improve water-related pore characteristics, supporting the need to evaluate biochar effects under specific soil and amendment contexts (Dayoub et al., 2025).

For Zn-related soil systems, current literature indicates that biochar may influence Zn retention and availability through its porous structure and associated nutrient interactions; therefore, adsorption measurements should be interpreted together with potential changes in availability (Ahmed et al., 2024).

1.2 Research Gap

Although previous studies describe Zn sorption and biochar-mediated changes in soil quality, information remains limited on how locally produced maize cob rind, pigeonpea stalk and cotton stalk biochars applied at different rates alter Zn adsorption affinity and Zn fractionation in contrasting red and black soils under controlled incubation conditions.

1.3 Objective of the Study

Therefore, this study aimed to evaluate the adsorption and distribution pattern of zinc in red and black soils amended with maize cob rind, pigeonpea stalk and cotton stalk biochars applied at different rates.

2. Materials and Methods

Representative soil samples of red Alfisol (plot no. 125), black Vertisol (plot no. 162) and biochars produced from plant residues such as maize cob rind, pigeonpea stalk and cotton stalk were collected from the Main Agricultural Research Station, Raichur. Biochar production was carried out using the drum method described by CRIDA, Hyderabad (Venkatesh et al., 2018). The crop residues, namely maize cob rind, pigeonpea stalk and cotton stalk, were chipped, air-dried and pyrolysed in a portable kiln (pyrolyser) under oxygen-limited conditions. The pyrolysis temperature was gradually increased at 10°C per min to a maximum of 300°C-450°C. The resulting biochars were allowed to cool to room temperature overnight. Representative samples of each biochar were collected and analysed for selected properties by following standard procedures and methods, and the data for the native soils and biochars used are shown in Table 1.

Five kilograms of each soil-biochar mixture were incubated in pre-water-soaked earthen pots. The mixtures were stirred and watered at regular intervals to maintain soil moisture approximately at near field-capacity level. Each treatment mixture had three replications (Table 2). Samples were collected 120 days after incubation, analysed for various physical and chemical parameters, and further used for the batch equilibration study of zinc adsorption and its distribution in soil.

Table 1. Physico-chemical properties of soils and biochars

Parameter	Red soil	Black soil	Maize cob rind biochar	Pigeonpea stock biochar	Cotton stock biochar
Physical properties					
Soil seperates (%)					
Sand	43.1	21.76			
Silt	29.9	26.21			
Clay	28.7	52.01			
Textural class	Sandy loam	Clay			
Maximum water holding capacity (%)	38.7	51.1	72.3	74.9	75.03
Bulk density (Mg m^{-3})	1.54	1.38	0.56	0.57	0.59
Porosity (%)	46.17	58.21	55.9	56.1	57.5
Chemical properties					
pH (1:2.5 soil water ratio)	6.71	8.12	9.51	9.49	9.34
Electrical conductivity (dSm^{-1})	0.2	0.31	2.89	2.98	3.41

Parameter	Red soil	Black soil	Maize cob rind biochar	Pigeonpea stock biochar	Cotton stock biochar
CEC (cmol(p$^+$) Kg^{-1}	20.12	54.79	13.3	15.3	16.2
Oganic Carbon (g kg-^{1})	3.78	4.36	67.8	71.5	73.4
Available nutrients (kg ha^{-1})					
Nitrogen	175.1	194.2	1090	1240	1160
Phosphorous	19.1	21.6	1170	1140	1190
Potassium	176.8	335.4	1380	1390	1420
Sulphur	18.02	4.45	2920	3120	3260
Exch. Ca (meq 100gm^{-1})	6.87	22.24	9370	9480	9710
Exch. Mg (meq 100gm^{-1})	1.9	15.95	250	250	280
DTPA extractable micronutrients (mg kg^{-1})					
Iron	9.86	9.6	122.7	126.5	128.3
Manganese	7.99	13.07	33.1	35.4	36.1
Copper	1.11	1.07	2.91	2.93	2.97
Zinc	0.46	0.65	17.01	17.24	17.62

Table 2. Treatments details

Soil type	Treatments	Quantity of biochar used (t ha-1)		
		MCRB	PPSB	CSB
Red soil	T1-Control	10 t ha^{-1}	10 t ha^{-1}	10 t ha^{-1}
Black soil	T2- Maize cob rind biochar @ 10 t ha-1	15 t ha^{-1}	15 t ha^{-1}	15 t ha^{-1}
	T3- Maize cob rind biochar @ 15t ha-1	20 t ha^{-1}	20 t ha^{-1}	20 t ha^{-1}
	T4- Maize cob rind biochar @ 20t ha-1			
	T5-Pigeonpea stock biochar@10t ha-1			
	T6-Pigeonpea stock biochar@15t ha-1			
	T7-Pigeonpea stock biochar@20t ha-1			
	T8-Cotton stock biochar @10t ha-1			
	T9-Cotton stock biochar @15t ha-1			
	T10-Cotton stock biocha @20t ha-1			

2.1 Zinc Sorption Study

The zinc sorption study was conducted using a laboratory batch experimentation technique. Two grams of each representative soil sample were weighed into each of six 50 ml polypropylene centrifuge tubes and equilibrated with 30 ml of 0.01 M $Ca(NO_3)_2.4H_2O$ containing six graded levels of zinc at 10, 25, 50, 100, 150 and 200 µM L-^{1} in the form of $Zn(NO_3)_2.6H_2O$. Calcium nitrate was used as the background electrolyte to eliminate non-specific adsorption of zinc and to saturate low-affinity sorption sites with calcium ions (Gray et al., 1998). After equilibrating solutions were added, the initial pH of the soil-solution suspensions was recorded. The soil suspensions were then shaken for 24 h using a horizontal mechanical shaker. Before centrifugation, the pH of the soil-solution suspensions was recorded again. After centrifugation at 7000 rpm for 15 min, the supernatant solution from each centrifuge tube was collected after filtration through Whatman No. 42 filter paper to remove particulates. The zinc concentration in the filtrate was determined using FAAS (Model: ContrAA700). The amount of zinc adsorbed by the soil was calculated from the difference between the amount of zinc added and the amount remaining in solution. All measurements were made in duplicate, and the average data were used for reporting. The adsorption data were interpreted using the linearised Freundlich and linearised Langmuir adsorption equations.

2.1.1 Linearized Freundlich equation

$$\log X/m = \log K_D + n \log C_e$$

where X/m = amount of zinc adsorbed per unit weight of soil in µM kg-^{1}, Ce = equilibrium solution concentration of zinc in µM L-^{1}, KD = distribution coefficient or adsorption affinity of zinc, and n = Freundlich equation constant.

2.1.2 Linearized Langmuir Equation

$$C_e/X/m = 1/K_b + C_e/b$$

where X/m = amount of zinc adsorbed per unit weight of soil in µM kg-^{1}, Ce = equilibrium solution concentration of zinc in µM L-^{1}, b = Langmuir adsorption maxima of zinc in µM kg-^{1}, and K = bonding energy constant.

2.2 Sequential Extraction of Native and Adsorbed Zinc in Samples

After adsorption, a four-step sequential extraction procedure (Walter and Cuevas, 1999) was used to study the distribution of native and adsorbed zinc at different equilibrating concentrations. This procedure was a modified version of that proposed by Emmerich et al., (1982). In the present study, the exchangeable fraction (EXC) included nonspecific adsorption of free and complexed zinc ions; the organic fraction (ORG) represented zinc held by complexation, adsorption and chelation processes; the inorganic or carbonate fraction (CAB) included surface-precipitated or co-precipitated zinc compounds, such as carbonates or hydroxides; and the residual fraction (RES) referred to zinc bound to sulphides or held within the crystal lattices of crystalline minerals in soils (Tessier et al., 1979; McBride, 1980).

3. Results and Discussion

The changes in soil properties following biochar application at different rates showed an increase in water-holding capacity and a decrease in bulk density. However, the effect was greater in black soil than in red soil, and among the biochars, CSB had a greater impact than the other biochars. The improvement in soil physical quality, in terms of bulk density (BD) and water-holding capacity (WHC), at different biochar application rates may be attributed to a significant increase in macropores and a reduction in soil strength (Hseu et al., 2014; Mukherjee and Lal, 2013). A moderate increase in soil pH, EC and OC, a small change in soil CEC, and comparatively higher available nutrient contents were also observed with increasing biochar application rate, irrespective of biochar type (Tables 3 and 4). Zhou et al., (2020) reported that soil amendment with maize stalk biochar increased soil pH, soil total organic carbon (TOC) and nutrient contents (TN and TP). Similarly, pigeonpea and cotton biochars have been reported to have soil amendment qualities suitable for soil application (Nataraja et al., 2021).

The adsorption studies of zinc in the two soil types after amendment with different biochars at different rates revealed changes in soil retention capacity and adsorption affinity. The amount of zinc adsorbed and the amount remaining in the equilibrium solution at different equilibrating concentrations are presented in Tables 5 and 6 for red and black soils, respectively. In general, plots with steep initial slopes that level off with subsequent increases in the equilibrium concentration of zinc, thereby producing a plateau or a linear section with a positive slope, are classified as L-type isotherms. These isotherms reflect a relatively high affinity between zinc and the soil surface and usually indicate chemisorption. In a few cases, the amount of zinc adsorbed increased linearly with an insignificant increase in its equilibrium concentration. Such plots in this study showed nearly vertical lines and were classified as H-type isotherms, suggesting very strong zinc-soil surface interactions; these are considered extreme cases of L-type isotherms (McBride, 1994). Different scales were used on the X and Y axes in the figures for the two soil types. The differences among isotherms for the treatments (T1 to T10) within each soil type were not clearly identifiable because of the small differences among amendment loading rates. Therefore, it may be generalised that both soils showed H-type isotherms. The increasing order of adsorption affinity for zinc in relation to isotherm type was L > L-2 > H. This indicates that black soil had greater adsorption affinity for added zinc than red soil. Similarly, Leckie and James (1974) observed simple L- or H-type isotherms for different metals. The more strongly adsorbed Pb and Cu, in particular, tended towards high-affinity (H-type) isotherms.

Simple adsorption isotherms were plotted using the equilibrium solution concentration of zinc (Ce) against the amount of zinc sorbed (X/m), as shown in Figs. 1 and 2 for red and black soils, respectively. In the present study, however, the plateau was not clearly established, mainly because of the low to moderately high zinc concentration range (10 to 200 µM L-^{1}); therefore, the Langmuir model did not fit the present adsorption data.

Freundlich isotherms were constructed for different treatments of the two soil types (Figs. 4 and 5 for red and black soils, respectively). The distribution coefficient (KD) for zinc was obtained from the regression of log Ce with log X/m and is presented in Table 7. The KD is analogous to the equilibrium constant of a chemical reaction and has been used to describe the partitioning of zinc between solid and liquid phases; therefore, higher KD values indicate greater zinc adsorption affinity or capacity. In contrast, low KD values indicate that most zinc in the system remains in solution and is therefore available for various chemical processes and plant uptake, whereas higher KD values reflect a greater affinity of solid soil components for zinc (Anderson and Christensen, 1988). Based on KD values, black soil had higher KD for zinc than red soil. Within each soil type, amended treatments had comparatively higher KD values than the respective controls (Figure 3). Among the treatments in both soils, higher biochar rates showed higher adsorption affinities (T4, T7 and T10). In all cases, the amount of zinc adsorbed increased with increasing equilibrating concentration. Black soil showed greater sorption for zinc than red soil. The amount of zinc sorbed, calculated from the equilibrium solution concentration, did not show large differences because of the low soil-to-solution ratio (1:15) used for equilibration. However, differences in zinc adsorption behaviour among soil types and treatments were evident from the isotherm parameters or constants. Sadat et al., (2019) also studied zinc adsorption in soils by interpreting adsorption data using the Langmuir and Freundlich equations and reported that the Freundlich equation fitted the sorption data better at higher zinc concentrations. In addition, Khayyun and Mseer (2019) observed that the Freundlich isotherm model described the adsorption process with a higher coefficient of determination (R2) than the Langmuir model at low initial heavy metal concentrations.

3.1 Distribution of Adsorbed Zinc

The sequential extraction of adsorbed zinc at different equilibrating concentrations helped explain the partitioning of zinc among geochemical phases and distinguish the predominant adsorption mechanisms in both soil types. The concentrations of zinc extracted in each fraction at different equilibrating concentrations are given in Tables 8 and 9, and the percentage distributions are shown in Figs. 6 and 7. In general, the data indicated that the distribution pattern of adsorbed zinc depended on soil type and zinc loading level, irrespective of biochar type. In each soil type, and at lower zinc additions, the differences in the amount of zinc extracted under each fraction among the treatments relative to the respective controls were small, but they became more distinct at higher zinc loadings. Among treatments within a soil type, unsystematic trends were observed in the concentrations of zinc extracted in different fractions. However, changes in the distribution pattern of adsorbed zinc were clearly observed, especially at higher zinc loadings. Most of the adsorbed Zn was found in the CAB or INORG fraction in both red and black soils, with comparatively higher values in black soil. At the highest Zn addition, 58.88% of adsorbed Zn was extracted in the CAB fraction in black soil, whereas 36.95% was extracted in red soil. Overall, zinc distribution in both soils followed the sequence CAB > RES > ORG > EXC. The data also showed that, at lower equilibrating concentrations, adsorbed zinc was distributed across all four fractions, whereas it tended to show preferential distribution at higher equilibrating concentrations. Therefore, to understand differences among treatments within each soil type and between soil types, most of the discussion was limited to zinc partitioning at the highest zinc addition (200 µM L-1). The concentration of zinc extracted in all four fractions increased linearly with increasing zinc loading rates in both soils. In red soil and its treatment mixtures, the percentage fractions of EXC and ORG zinc increased with higher zinc loading rates, whereas the percentage fractions of CAB and RES zinc decreased with increasing zinc loading rates. In black soil, at lower zinc loadings, the percentage fractions of zinc in the EXC, ORG and CAB fractions were comparatively lower and increased with higher zinc loading rates, except for the RES fraction, which decreased at high zinc loadings. These observations confirm that, irrespective of soil type and biochar, a small fraction of added zinc was retained in moderately available forms, and this tendency increased largely with the level of zinc loading, although the distribution pattern was only slightly affected at higher zinc loadings. Different soil constituents contributed to zinc adsorption through different mechanisms; however, at higher zinc loadings, zinc adsorption occurred preferentially through precipitation, possibly as carbonates. Adhikari and Rattan (2007) reported that more than 90% of total Zn occurred in relatively inactive clay lattice and other mineral-bound forms (RES), while only a small fraction occurred as WS, EX, OM, AFe-OX and CFe-OX forms. Comparably, the concentration of exchangeable Zn decreased significantly by nearly 60% and 54% with the application of 1.5% and 3% biochar, respectively, to agricultural soil. Nevertheless, carbonate Zn concentration decreased significantly by 44% after 3% biochar was applied (Zahedifar, 2017).

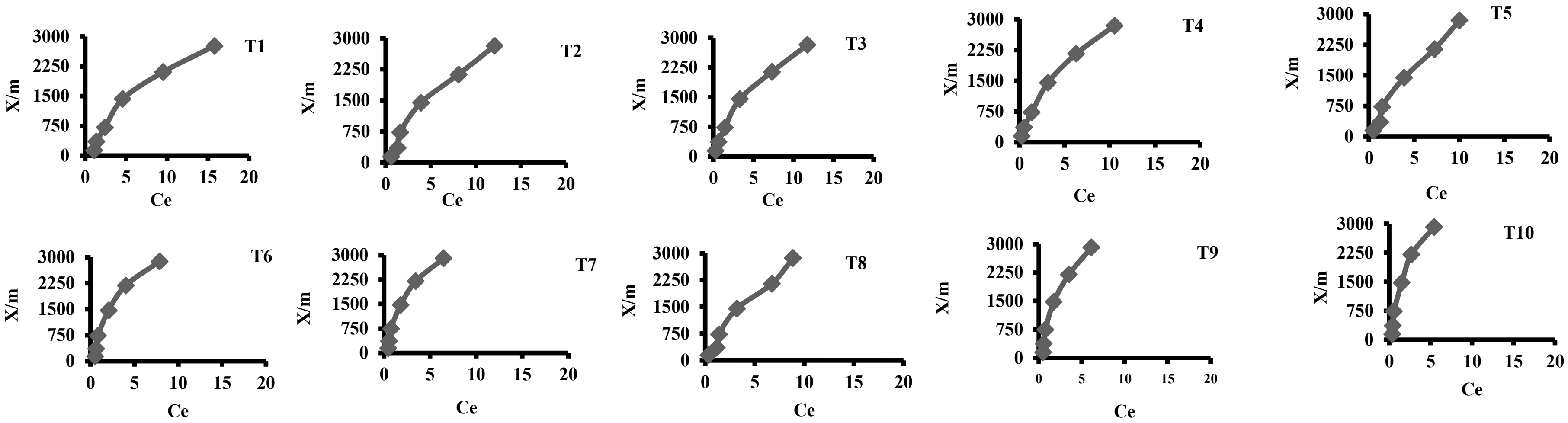


Fig. 1. Adsorption isotherms for zinc in red soil

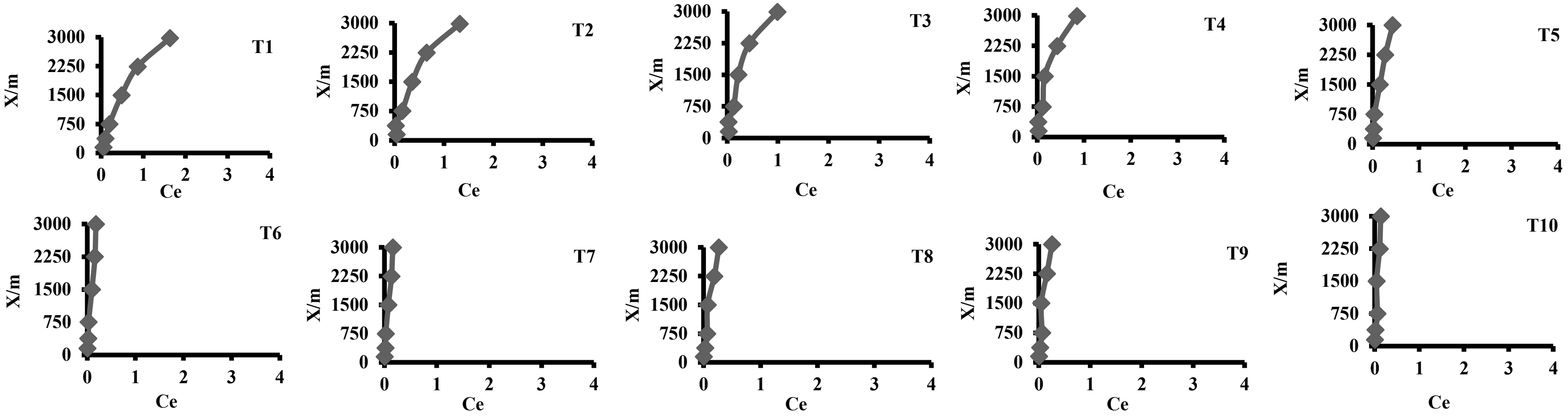


Fig. 2. Adsorption isotherms for zinc in black soil

C_e = Equilibrium solution concentration of zinc in µM L^{-1}X/m = Amount of zinc adsorbed per unit weight of soil in µM Kg^{-1}

Note: *T_1 - Control, T_2 - MCRB @ 10 t ha^{-1}, T_3 - MCRB @ 15 t ha^{-1}, T_4 – MCRB @ 20 t ha^{-1}, T_5 - PPSB @ 10 t ha^{-1}, T_6 - PPSB @ 15 t ha^{-1}, T_7 - PPSB @ 20 t ha^{-1}, T_8 – CSB @ 10 t ha^{-1}, T_9 – CSB @ 15 t ha^{-1}, T_{10} - CSB @ 20 t ha^{-1}*

Table 3. Effect of different types and levels of biochars on physico-chemical parameters of red soil

Treatments	**MWHC**	**BD**	**Porosity**	**pH**	**EC**	**OC**	**CEC**	**Available nutrients (kg ha^{-1})**				**Exch. nutrients**		**Available micronutrients (mg kg^{-1})**			
												Exch. nutrients (meq $100gm^{-1}$)					
	(%)	**(Mgm^{-3})**	**(%)**		**(dsm^{-1})**	**(g kg^{-1})**	**(cmol (p+)kg^{-1})**	**N**	**P_2O_5**	**K_2O**	**S**	**Ca**	**Mg**	**Cu**	**Fe**	**Mn**	**Zn**
T_1-Contol	39.3	1.58	48.46	6.72	0.21	3.78	20.19	176.32	23.12	178.5	20.82	7	2.2	1.11	9.89	8.02	0.51
T_2-MCRB @ 10 t ha^{-1}	41.7	1.49	49.27	7.59	0.23	4.05	20.42	184.87	29.46	185.4	22.16	9	3	2.16	10.3	8.34	0.56
T_3-MCRB @ 15 t ha^{-1}	42.4	1.48	50.81	8.03	0.31	4.08	20.55	189.54	31.76	209.2	22.82	9.3	2.9	3.36	11.6	8.64	0.6
T_4-MCRB @ 20 t ha^{-1}	43.2	1.43	51.21	8.27	0.41	4.14	23.38	194.32	32.18	250.5	23.37	9.6	3.1	3.65	12.8	9.48	0.63
T_5-PPSB @ 10 t ha^{-1}	42.1	1.47	49.04	7.57	0.26	4.35	31.13	187.5	30.17	195	22.25	10.3	3.1	2.35	11	8.42	0.57
T_6-PPSB @ 15 t ha^{-1}	42.9	1.45	52.89	7.94	0.33	4.41	43.17	191.41	32.59	221.4	22.93	10.6	3.9	3.52	13.5	8.78	0.62
T_7-PPSB @ 20 t ha^{-1}	44.9	1.4	55.84	8.12	0.45	4.47	43.56	198.43	33.46	282.5	23.76	10.8	3.5	3.98	14.8	9.52	0.67
T_8-CSB @ 10 t ha^{-1}	43.3	1.44	49.17	7.35	0.28	4.5	54.58	189.32	31.87	213.9	22.89	11.2	3.7	2.48	12.6	8.49	0.59

Treatments	MWHC	BD	Porosity	pH	EC	OC	CEC	Available nutrients (kg ha^{-1})				Exch. nutrients		Available micronutrients (mg kg^{-1})			
												Exch. nutrients (meq 100gm^{-1})					
	(%)	(Mgm^{-3})	(%)		(dsm^{-1})	(g kg^{-1})	(cmol (p+)kg^{-1})	N	P_2O_5	K_2O	S	Ca	Mg	Cu	Fe	Mn	Zn
T_9-CSB @15 t ha^{-1}	43.7	1.42	52.67	7.89	0.39	4.56	56.62	194.02	33.46	246.8	23.07	11.5	4.1	3.77	14.8	8.81	0.63
T_{10}-CSB @ 20 t ha^{-1}	45.8	1.39	55.92	8.03	0.48	4.59	58.95	199.65	34.97	293.7	23.96	12.3	4.2	4.12	15.7	9.56	0.69

Table 4. Effect of different types and levels of biochars on physico-chemical parameters of black soil

Treatments	MWHC	BD	Porosity	pH	EC	OC	CEC	Available nutrients (kg ha^{-1})				Exch. nutrients (meq 100gm^{-1})		Available micronutrients (mg kg^{-1})			
	(%)	(Mgm^{-3})	(%)		(dsm^{-1})	(g kg^{-1})	(cmol (p+) kg^{-1})	N	P_2O_5	K_2O	S	Ca	Mg	Cu	Fe	Mn	Zn
T_1-Contol	52.3	1.37	59.07	8.16	0.32	4.22	55.63	199.6	28..3	339.1	22.63	16.8	4.95	1.07	9.6	15.26	0.68
T_2-MCRB @ 10 t ha^{-1}	54.5	1.35	59.09	8.24	0.36	4.83	56.63	210.4	32.03	356.3	24.73	17.3	5.15	1.36	12.3	17.34	0.8
T_3-MCRB @ 15 t ha^{-1}	55.7	1.34	59.63	8.27	0.41	4.91	56.93	229.8	34.17	380.7	25.35	17.3	5.32	1.65	14.7	19.47	0.99
T_4-MCRB @ 20 t ha^{-1}	56.9	1.32	59.85	8.31	0.52	4.96	57.33	235.4	35.38	391.6	25.95	22	5.75	2.16	18.7	20.48	1.04
T_5-PPSB @ 10 t ha^{-1}	55.4	1.34	59.44	8.23	0.39	4.87	57.71	226.2	33.46	363.7	24.87	17.6	6.14	1.45	22.8	23.52	0.84
T_6-PPSB @ 15 t ha^{-1}	56.9	1.33	59.84	8.25	0.43	4.94	58.01	247.8	35.39	393.6	25.78	17.8	6.25	2.16	27.5	27.68	1.01
T_7-PPSB @ 20 t ha^{-1}	57.3	1.31	60.85	8.29	0.56	4.98	59.45	274.6	36.84	402.5	26.02	18.8	6.48	2.48	30	28.12	1.08
T_8-CSB @ 10 t ha^{-1}	56.3	1.32	60.12	8.21	0.4	4.91	58.75	239.2	34.12	374.4	25.12	18..5	6.25	1.89	30	26.77	0.87
T_9-CSB @15 t ha^{-1}	57.1	1.31	61.71	8.24	0.46	5.01	59.12	268.6	35.78	411.5	25.98	18.8	6.31	2.5	32	28.2	1.03
T_{10}-CSB @ 20 t ha^{-1}	58.9	1.3	63.71	8.28	0.59	5.13	59.87	293.2	36.16	426.2	26.25	19	7.01	2.8	33.7	29.3	1.13

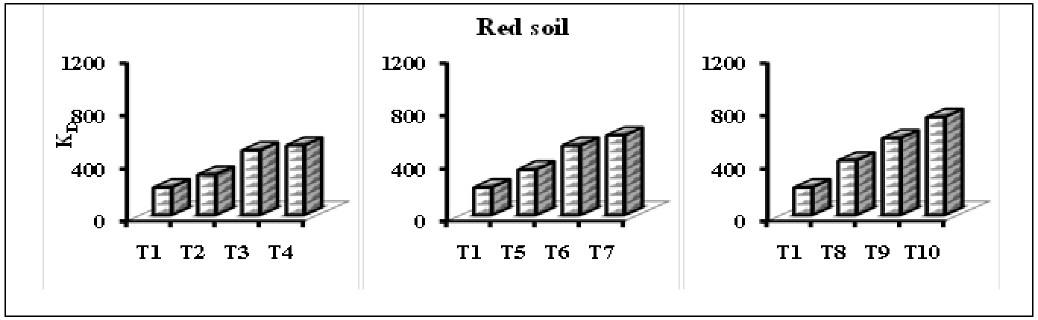
Table 5. Adsorption data of zinc in different treatments at different equilibrating concentrations in red soil

Treatments	Zinc Equilibrating Concentrations (µM L^{-1})											
	10		25		50		100		150		200	
	Ce	X/m	Ce	X/m	Ce	X/m	Ce	X/m	Ce	X/m	Ce	X/m
T_1-Contol	1.095	133.6	1.389	354.2	2.426	713.6	4.595	1431.1	9.519	2107.2	15.79	2763
T_2-MCRB @ 10 t ha^{-1}	0.578	141.3	1.334	355.1	1.591	726.1	3.911	1441.4	8.082	2128.7	12.09	2818.7
T_3-MCRB @ 15 t ha^{-1}	0.252	146.1	0.637	365.4	1.423	728.6	3.291	1450.7	7.299	2140.5	11.73	2824
T_4-MCRB @ 20 t ha^{-1}	0.249	146.2	0.513	367.3	1.356	729.6	3.156	1452.7	6.282	2155.7	10.22	2846.7
T_5-PPSB @ 10 t ha^{-1}	0.473	142.9	0.754	363.7	1.238	731.4	3.427	1448.6	7.236	2141.5	9.014	2864.8

Treatments	Zinc Equilibrating Concentrations (µM L^{-1})											
	10		25		50		100		150		200	
	Ce	X/m	Ce	X/m	Ce	X/m	Ce	X/m	Ce	X/m	Ce	X/m
T_6-PPSB @ 15 t ha^{-1}	0.172	147.4	0.623	365.7	0.938	735.9	2.363	1464.5	5.024	2174.6	8.659	2870.1
T_7-PPSB @ 20 t ha^{-1}	0.087	148.6	0.395	369.1	0.795	738.1	1.722	1474.2	4.739	2178.9	5.763	2913.6
T_8-CSB @ 10 t ha^{-1}	0.228	146.5	0.298	370.5	0.796	738.1	1.804	1483.7	3.741	2193.9	6.851	2897.2
T_9-CSB @15 t ha^{-1}	0.142	147.8	0.282	370.8	0.569	741.4	1.731	1474.1	3.512	2197.3	6.121	2908.2
T_{10}-CSB @ 20 t ha^{-1}	0.086	148.7	0.142	372.9	0.489	742.7	1.518	1477.2	2.696	2209.6	5.419	2918.7

Table 6. Adsorption data of zinc in different treatments at different equilibrating concentrations in black soil

Treatments	Zinc Equilibrating Concentrations (µM L^{-1})											
	10		25		50		100		150		200	
	Ce	X/m	Ce	X/m	Ce	X/m	Ce	X/m	Ce	X/m	Ce	X/m
T_1-Contol	0.055	149.17	0.103	373.45	0.197	747.04	0.482	1492.7	0.8632	2237.1	1.631	2975.5
T_2-MCRB @ 10 t ha^{-1}	0.045	149.32	0.024	374.64	0.155	747.67	0.356	1494.6	0.6504	2240.3	1.319	2980.2
T_3-MCRB @ 15 t ha^{-1}	0.029	149.56	0.021	374.68	0.128	748.08	0.219	1496.7	0.4379	2243.4	0.988	2985.2
T_4-MCRB @ 20 t ha^{-1}	0.023	149.65	0.018	374.73	0.119	748.21	0.159	1497.6	0.4262	2243.6	0.846	2987.3
T_5-PPSB @ 10 t ha^{-1}	0.015	149.77	0.031	374.53	0.042	749.37	0.159	1497.6	0.2758	2245.9	0.432	2993.5
T_6-PPSB @ 15 t ha^{-1}	0.007	149.89	0.023	374.65	0.028	749.58	0.096	1498.6	0.1589	2247.6	0.179	2997.3
T_7-PPSB @ 20 t ha^{-1}	0.004	149.94	0.019	374.71	0.025	749.62	0.076	1498.9	0.1347	2248	0.159	2997.6
T_8-CSB @ 10 t ha^{-1}	0.005	149.92	0.028	374.58	0.065	749.03	0.071	1498.9	0.1886	2247.2	0.269	2995.9
T_9-CSB @15 t ha^{-1}	0.003	149.95	0.026	374.61	0.063	749.05	0.048	1499.3	0.1565	2247.7	0.258	2996.1
T_{10}-CSB @ 20 t ha^{-1}	0.002	149.97	0.019	374.71	0.061	749.08	0.045	1499.3	0.1108	2248.3	0.135	2997.9



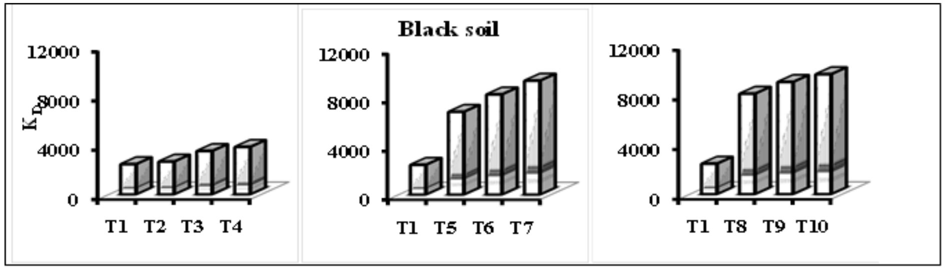


Fig. 3. Linearized Freundlich's Distribution coefficient values for zinc in various treatments in red and black soil

Note: T1 - Control, T2 - MCRB @ 10 t ha-1, T3 - MCRB @ 15 t ha-1, T4 – MCRB @ 20 t ha-1, T5 - PPSB @ 10 t ha-1, T6 - PPSB @ 15 t ha-1, T7 - PPSB @ 20 t ha-1, T8 – CSB @ 10 t ha-1, T9 – CSB @ 15 t ha-1, T10 - CSB @ 20 t ha-

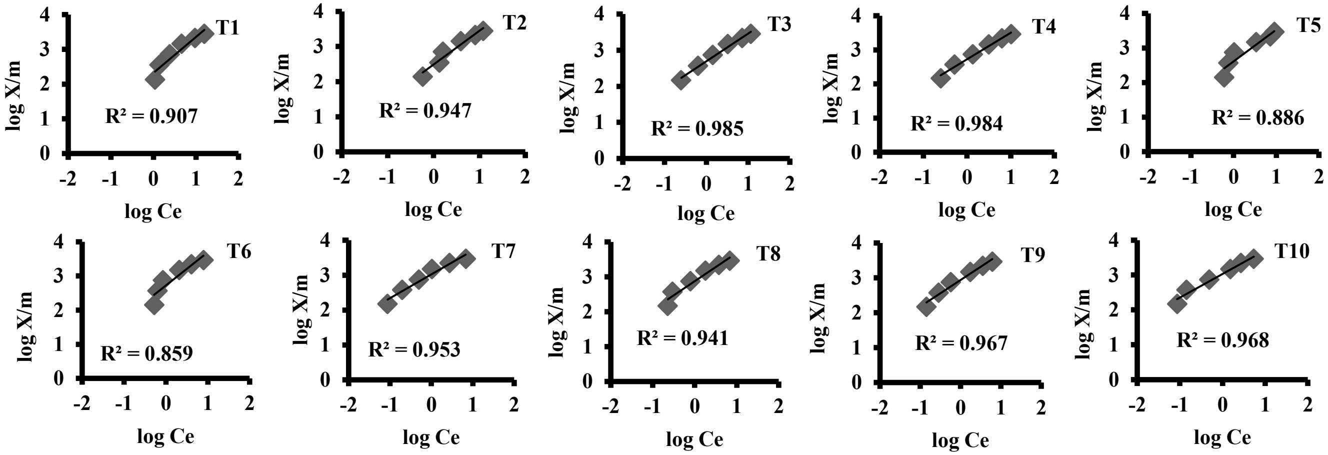


Fig. 4. Linearized Freundlich adsorption isotherms for red soil

Note: *T_1 - Control,*
T_2 - MCRB @ 10 t ha^{-1},
T_3 - MCRB @ 15 t ha^{-1}, T_4 – MCRB @ 20 t ha^{-1},
T_5 - PPSB @ 10 t ha^{-1}, T_6 - PPSB @ 15 t ha^{-1},
T_7 - PPSB @ 20 t ha^{-1}, T_8 – CSB @ 10 t ha^{-1},
T_9 – CSB @ 15 t ha^{-1}, T_{10} - CSB @ 20 t ha^{-1}

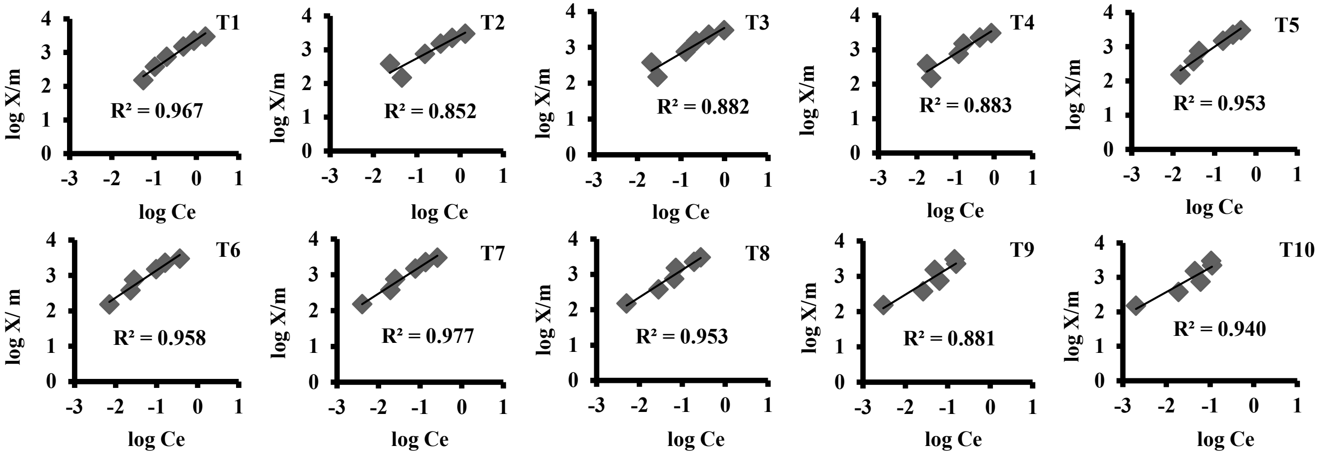


Fig. 5. Linearized Freundlich adsorption isotherms for black soil

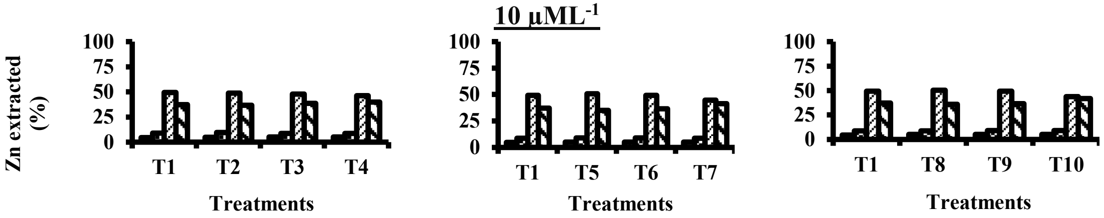
Table 7. Linearized Freundlich's distribution coefficient values for zinc in red and black soils

Treatments	**Red soil** **K_D-Zn**	**Black soil** **K_D-Zn**
T_1-Contol	208.9	2437.8
T_2-MCRB @ 10 t ha^{-1}	307.6	3006.1
T_3-MCRB @ 15 t ha^{-1}	490.9	4045.8.
T_4-MCRB @ 20 t ha^{-1}	528.4	4456.6
T_5-PPSB @ 10 t ha^{-1}	415	6998.4
T_6-PPSB @ 15 t ha^{-1}	622.3	9418.9
T_7-PPSB @ 20 t ha^{-1}	824.1	10519.6
T_8-CSB @ 10 t ha^{-1}	749.9	8629.8
T_9-CSB @15 t ha^{-1}	869	9840.1
T_{10}-CSB @ 20 t ha^{-1}	1074	11220

Table 8. Distribution of adsorbed zinc (µM kg^{-1}) in red soiltreated with different biocharsat various equilibrating concentrations

Treatments	**10 µML^{-1}**				**25 µML^{-1}**				**50 µML^{-1}**			
	EXC	**ORG**	**CAB**	**RES**	**EXC**	**ORG**	**CAB**	**RES**	**EXC**	**ORG**	**CAB**	**RES**
T_1-Contol	0.64	1.21	6.74	5.08	1.64	3.95	12.78	10.33	2.97	7.30	18.86	15.22
T_2-MCRB @ 10 t ha^{-1}	0.72	1.38	7.05	5.28	1.90	4.21	13.25	10.76	3.25	7.87	19.49	15.81
T_3-MCRB @ 15 t ha^{-1}	0.85	1.44	8.08	6.52	1.96	4.49	13.74	11.12	3.44	8.15	19.65	16.01
T_4-MCRB @ 20 t ha^{-1}	0.93	1.55	8.38	7.24	1.98	4.72	14.60	11.31	3.78	8.60	20.42	16.78
T_5-PPSB @ 10 t ha^{-1}	0.78	1.39	7.78	5.37	1.91	4.29	13.41	11.09	3.39	8.10	19.84	15.95
T_6-PPSB @ 15 t ha^{-1}	0.89	1.56	8.51	6.35	1.96	4.59	14.03	11.54	3.65	8.54	19.68	16.65
T_7-PPSB @ 20 t ha^{-1}	1.03	1.74	8.86	8.22	1.98	4.94	15.18	12.27	3.87	8.99	20.11	17.18
T_8-CSB @ 10 t ha^{-1}	0.85	1.44	8.31	5.91	1.93	4.56	14.25	11.13	3.59	8.43	19.23	17.61
T_9-CSB @15 t ha^{-1}	0.92	1.59	8.77	6.51	1.97	5.02	15.13	11.87	3.86	8.92	19.68	17.89
T_{10}-CSB @ 20 t ha^{-1}	1.09	1.90	9.09	8.73	2.00	5.29	15.64	12.28	4.09	9.48	21.19	18.19

Treatments	**100 µML^{-1}**				**150 µML^{-1}**				**200 µML^{-1}**			
	EXC	**ORG**	**CAB**	**RES**	**EXC**	**ORG**	**CAB**	**RES**	**EXC**	**ORG**	**CAB**	**RES**
T_1-Contol	4.72	11.18	23.10	18.68	10.29	20.03	35.74	27.66	18.95	35.22	55.10	39.84
T_2-MCRB @ 10 t ha^{-1}	4.87	11.82	23.20	18.91	10.73	20.65	36.20	27.97	19.03	35.35	55.23	39.95
T_3-MCRB @ 15 t ha^{-1}	4.92	12.01	23.43	19.06	11.16	20.89	36.36	28.13	19.13	35.81	55.81	40.04
T_4-MCRB @ 20 t ha^{-1}	5.33	12.90	23.52	20.45	11.47	21.65	36.94	28.72	19.32	36.18	56.02	40.48
T_5-PPSB @ 10 t ha^{-1}	4.93	12.07	23.70	19.13	10.89	20.69	36.50	28.16	19.16	35.42	55.43	41.13
T_6-PPSB @ 15 t ha^{-1}	5.15	13.32	23.96	20.12	11.41	20.01	36.59	28.36	19.21	35.91	55.90	41.24
T_7-PPSB @ 20 t ha^{-1}	5.54	12.51	23.98	21.64	11.61	21.87	37.45	28.55	19.44	36.32	56.46	41.56
T_8-CSB @ 10 t ha^{-1}	5.12	12.43	23.90	19.73	10.99	20.14	36.83	28.16	19.23	35.73	55.64	41.24
T_9-CSB @15 t ha^{-1}	5.26	12.69	24.01	20.31	11.59	20.19	36.81	28.59	19.47	35.99	56.10	41.38
T_{10}-CSB @ 20 t ha^{-1}	5.81	13.89	24.50	22.74	11.85	21.92	37.68	28.79	19.75	36.43	56.69	41.71



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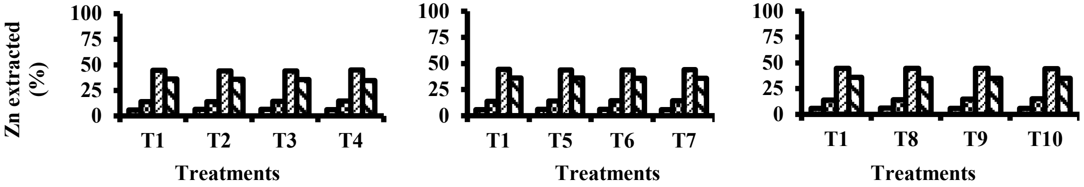

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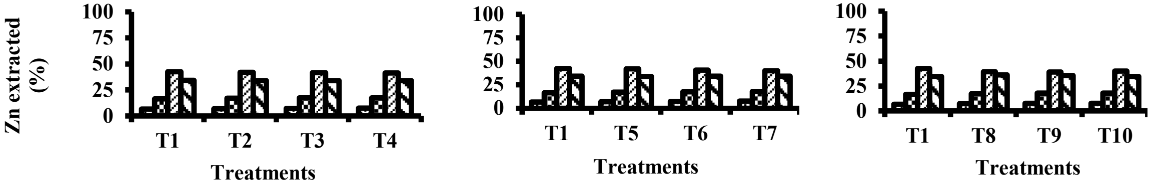

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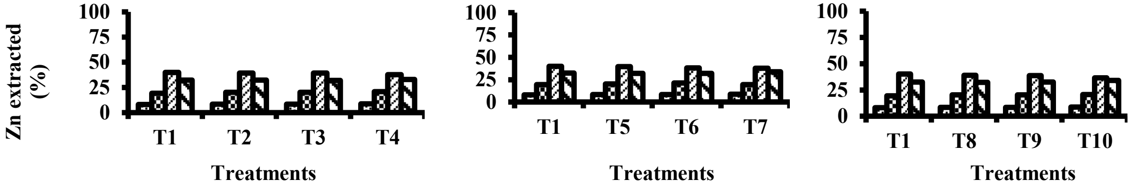

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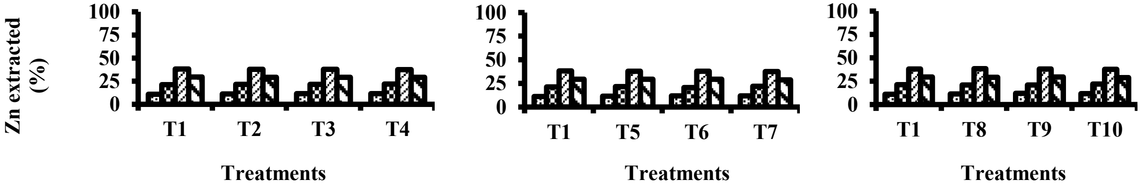


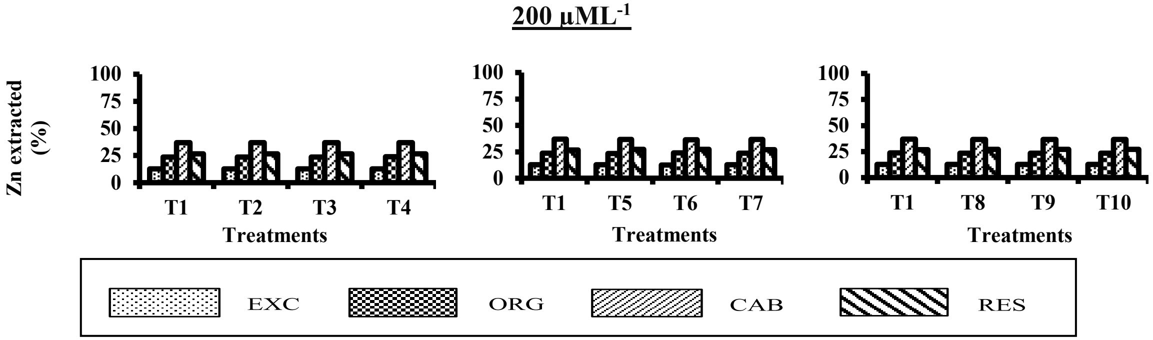


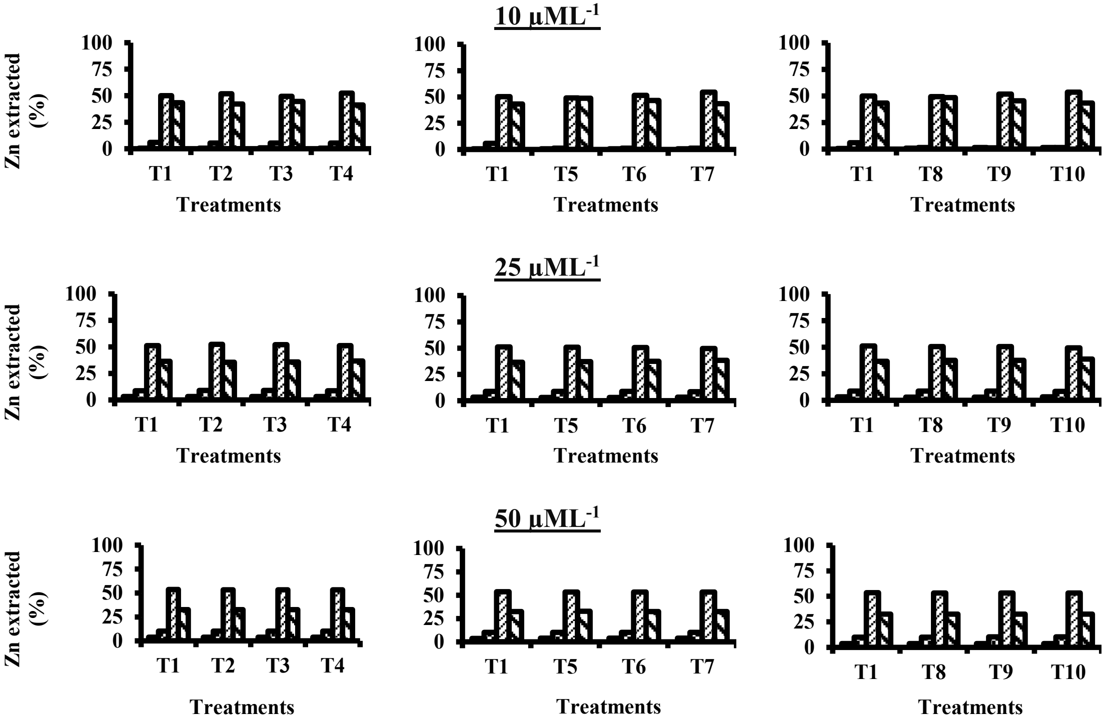
Fig. 6. Percentages of zinc extracted through sequential extraction at different equilibrating concentrations in red soil

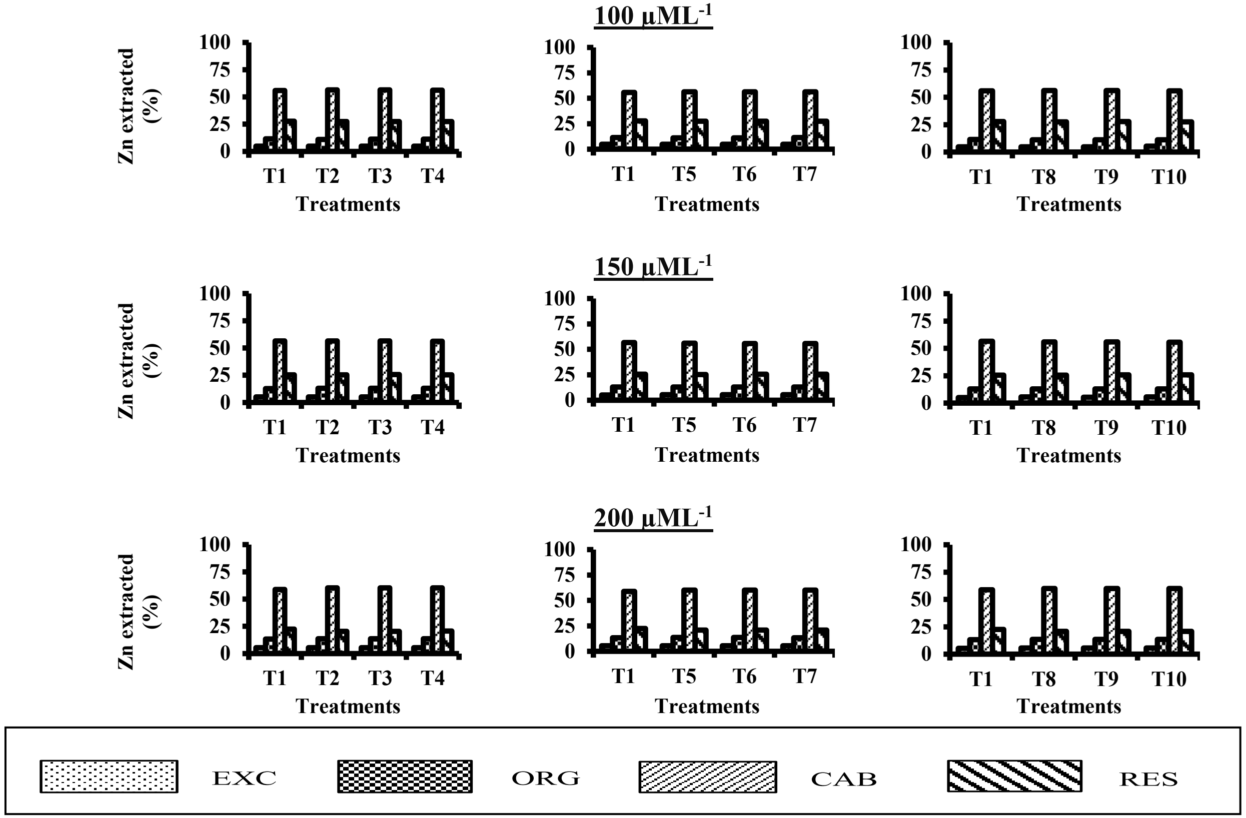
Table 9. Distribution of adsorbed zinc (µM kg^{-1}) in black soil treated with different biocharsat various equilibrating concentrations

Treatments	10 µML^{-1}				25 µML^{-1}				50 µML^{-1}			
	EXC	ORG	CAB	RES	EXC	ORG	CAB	RES	EXC	ORG	CAB	RES
T$_1$-Contol	0.13	1.20	8.80	10.18	1.21	3.17	18.49	13.20	3.14	8.35	44.35	27.00
T$_2$-MCRB @ 10 t ha^{-1}	0.14	1.11	8.97	10.97	1.21	3.37	19.69	13.34	3.17	8.42	44.41	27.15
T$_3$-MCRB @ 15 t ha^{-1}	0.16	1.24	10.05	11.15	1.22	3.37	19.89	13.63	3.21	8.56	44.53	27.23
T$_4$-MCRB @ 20 t ha^{-1}	0.16	1.34	10.12	12.87	1.27	3.44	20.01	14.40	3.26	8.60	44.74	27.24
T$_5$-PPSB @ 10 t ha^{-1}	0.15	0.28	10.09	10.17	1.22	3.41	19.75	14.48	3.19	8.49	44.45	27.18
T$_6$-PPSB @ 15 t ha^{-1}	0.16	0.27	10.27	11.34	1.22	3.43	19.92	14.75	3.24	8.59	44.65	27.28
T$_7$-PPSB @ 20 t ha^{-1}	0.17	0.31	10.31	12.92	1.31	3.46	20.11	15.56	3.28	8.59	44.74	27.37
T$_8$-CSB @ 10 t ha^{-1}	0.18	0.29	10.18	10.38	1.23	3.42	19.82	14.78	3.19	8.50	44.67	27.33
T$_9$-CSB @15 t ha^{-1}	0.33	0.29	10.40	11.78	1.23	3.45	19.95	14.88	3.25	8.59	44.79	27.38
T$_{10}$-CSB @ 20 t ha^{-1}	0.36	0.35	10.53	12.99	1.34	3.47	20.27	15.95	3.28	8.62	45.11	27.51

Treatments	100 µML^{-1}				150 µML^{-1}				200 µML^{-1}			
	EXC	ORG	CAB	RES	EXC	ORG	CAB	RES	EXC	ORG	CAB	RES
T$_1$-Contol	6.17	14.83	71.42	35.48	10.10	25.82	113.23	50.93	20.09	49.63	220.69	84.35
T$_2$-MCRB @ 10 t ha^{-1}	6.18	14.29	72.74	35.37	10.13	26.09	113.36	51.25	20.12	49.40	220.01	74.73
T$_3$-MCRB @ 15 t ha^{-1}	6.19	14.58	72.99	35.68	10.16	26.31	113.74	51.54	20.16	49.71	220.32	74.86
T$_4$-MCRB @ 20 t ha^{-1}	6.20	14.78	73.06	35.82	10.22	26.52	113.98	51.61	20.21	49.84	220.59	75.24
T$_5$-PPSB @ 10 t ha^{-1}	6.19	14.42	72.81	35.57	11.17	26.39	113.39	51.46	20.17	49.73	220.23	75.82

Treatments	**10 µML^{-1}**				**25 µML^{-1}**				**50 µML^{-1}**			
	EXC	**ORG**	**CAB**	**RES**	**EXC**	**ORG**	**CAB**	**RES**	**EXC**	**ORG**	**CAB**	**RES**
T_6-PPSB @ 15 t ha^{-1}	6.22	14.64	73.05	35.80	11.19	26.48	113.85	52.25	20.22	49.85	220.47	75.99
T_7-PPSB @ 20 t ha^{-1}	6.25	14.81	73.40	35.93	11.26	26.61	113.99	52.66	20.24	49.01	220.62	76.36
T_8-CSB @ 10 t ha^{-1}	6.30	14.55	72.99	35.85	11.17	26.48	113.43	51.97	20.20	49.89	220.36	75.96
T_9-CSB @15 t ha^{-1}	6.24	14.75	73.16	36.15	11.21	26.60	113.97	52.52	20.24	49.92	220.53	76.11
T_{10}-CSB @ 20 t ha^{-1}	6.97	14.81	73.64	36.34	11.28	26.66	114.10	52.57	20.29	50.01	220.71	76.47




100 µML^{-1}

150 µML^{-1}

200 µML^{-1}

Fig. 7. Percentages of zinc extracted through sequential extraction at different equilibrating concentrations in black soil

4. Conclusion

The study showed that amendment of red and black soils with maize cob rind, pigeonpea stalk and cotton stalk biochars altered selected soil properties and influenced zinc adsorption behaviour. Biochar application increased water-holding capacity, organic carbon, cation exchange capacity, pH and available nutrients, while reducing bulk density. The magnitude of change generally increased with the biochar application rate. Zinc adsorption was better described by the Freundlich adsorption equation than by the Langmuir equation under the concentration range used in the study. Black soil recorded higher Freundlich distribution coefficient values than red soil, indicating stronger zinc retention capacity. Among the biochars, cotton stalk biochar generally produced the highest zinc adsorption, followed by pigeonpea stalk biochar and maize cob rind biochar. Sequential extraction indicated that native zinc was mainly present in less mobile fractions, whereas added zinc at higher loading shifted more towards carbonate-bound and other surface-associated forms. These findings suggest that biochar amendments can increase zinc retention in soil, but the magnitude of the effect depends on soil type, biochar source and application rate. Further field-based studies are needed to relate zinc adsorption behaviour to crop uptake, zinc availability and long-term soil quality under repeated biochar application.

5. Limitations

This study was limited to laboratory incubation, batch adsorption and sequential extraction experiments using two soil types and three biochar sources. The results therefore describe zinc retention and distribution under controlled conditions and may not fully represent field behaviour under cropping, irrigation, drainage and seasonal variation. The experiment did not include plant uptake studies, crop yield response, leaching assessment or long-term repeated biochar application. Zinc availability to plants was inferred from adsorption and fractionation patterns rather than measured directly through crop growth or tissue analysis. The study also used a limited zinc concentration range and did not fully establish Langmuir adsorption maxima. Biochar properties were measured, but additional characterization, such as surface area, functional groups and ash composition, would strengthen interpretation of adsorption mechanisms. Further multi-season field studies with plant uptake data and long-term monitoring of salinity, zinc availability and soil quality are required before broad agricultural recommendations can be made.

Declaration of AI Use

This manuscript was prepared through the combined contributions of all author(s), including contributions to the study design, data, content development, results, interpretation, and related scholarly work. The author(s) acknowledge the use of Grammarly and Chat gpt to assist with grammar checking, language refinement, reference formatting. These AI-assisted tools were not used as authors and did not replace the intellectual contributions or scholarly judgment of the author(s). All AI-assisted outputs, including content, references, and interpretations, were carefully reviewed, revised, verified, and approved by the author(s). The author(s) accept full responsibility for the accuracy, integrity, and final content of the manuscript.

Competing Interests

Authors have declared that no competing interests exist.

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