Biochar application in a metal contaminated soil reduce heavy metal accumulation in different parts of Rice

Abstract

Heavy metal contamination in agricultural field is a challenging aspect globally. Various methods are employed to address the issue; biochar among the most cost-effective and promising one. Our study encompasses biochar preparation from Parthenium, a noxious weed of agricultural field, and its subsequent modification using ferric chloride and orthophosphoric acid. Results reveal that more than 20% reduction of Pb, Cd and Ni in Rice roots under different biochar treatments. Moreover, greater than 30% reduction of abovementioned heavy metals in Rice grains is also noted. So, it can be concluded from our study that biochar application to a metal contaminated soil can be a promising approach to reduce metal accumulation in different parts of rice and subsequently addressing the adverse effect of it in human body.

Introduction

The presence of heavy metals (HMs) in soil and water poses a significant threat to both ecosystems and human health. This issue primarily stems from the discharge of metal-contaminated wastewater by industries like metallurgy, steel production, tanneries, and cement manufacturing (**Crisostomo et al. 2016**). To combat this problem, one effective method of metal removal is through adsorption process. This approach is known for its high efficiency, operational simplicity, and economic benefits, while avoiding the generation of sludge (**Wu and Zhao 2011**). Biochar, with its advantageous characteristics like liming effect, extensive surface area, high cation exchange capacity, porous structure, negatively charged surface, and oxygen-containing functional groups, has the potential to remediate soil contaminated with metals. Biochar, with its extensive surface area and reactivity, has gained importance as an adsorbent for removing metals from soil and wastewater (**Beiyuan et al. 2020**). Notably, iron-based materials have been a focal point for environmental applications and the treatment of various pollutants in recent days (**Niu et al. 2011**). In their study, **Singaraj et al. (2019)** demonstrated that use of humic acid coated iron oxide nanoparticle was able to sorb Cr which was not easily released even after acid-alkali treatment. Recent research focuses on enhancing ability of biochar to immobilize HMs through modifications. This includes introduction of organic or inorganic materials, such as Fe-compounds (**Bian et al., 2018**) and phosphate materials (**Zhang et al., 2020**), to improve its performance in HM immobilization. In a study by **Yang et al. (2021)**, it was found that incorporating phosphorus-rich biochar derived from pig carcasses into paddy soils might be a promising technique for reducing Pb risks to human health. Additionally, biochars derived from iron-rich green waste were effective in immobilizing Cd and minimizing its impact in paddy soils and the environment. Rice, a crucial cereal for half the global population, can accumulate heavy metals (HMs), posing a significant source of HMs in the human body (**Li et al. 2020**). In this respect, urgent attention addressing the simultaneous immobilization and reduction of bioavailability of HMs in paddy soils is crucial for sustainable soil management and safeguarding human health. Considering the aforementioned possibilities, primary aim of our study to reduce heavy metal accumulation in different parts of Rice cultivated in a heavy metal contaminated soil through graded dose of simple and modified biochar administration.

Materials and methods

Pot experiment details

Heavy metal contaminated soil is collected from industrial wastewater irrigated farmers field near Jajmau area in Kanpur, India and the soil was transported to Glass house of Institute of Agricultural Sciences, Banaras Hindu University. The soil was slightly alkaline (pH = 7.6 in 1: 2 :: soil : solution), non-saline (EC = 1.8 dS m^{-1}) with loamy texture. The soil contains 200 ppm Pb, 100 ppm Ni and 17 ppm Cd which is much higher than the permissible limit of 100, 50 and 3 ppm for Pb, Ni and Cd respectively. Subsequently, the soil was air-dried, ground and sieved through 2 mm sieve and filled up to the plastic lined 10 kg pot after uniform mixing with biochar according to the treatments detailed. Rice seedlings (HUR-105) was transplanted after flooding the soil.

Treatment details

The treatments used in the experiment is outlined as: T1: Control, T2: Raw biochar @ 5 t ha^{-1}, T3: Raw biochar @ 7.5 t ha^{-1}, T4: Raw biochar @ 10 t ha^{-1}, T5: Phosphoric acid modified biochar @ 5 t ha^{-1}, T6: Phosphoric acid modified biochar @ 7.5 t ha^{-1}, T7: Phosphoric acid modified biochar @ 10 t ha^{-1}, T8: Iron chloride modified biochar @ 5 t ha^{-1}, T9: Iron chloride modified biochar @ 7.5 t ha^{-1}, T10: Iron chloride modified biochar @ 10 t ha^{-1}.

Biochar preparation and modification

Succulent plants of Parthenium were harvested, cleansed, chopped, sundried, and subjected to biochar preparation as outlined by **Venkatesh et al. (2013)**. Subsequently, the prepared biochar was sieved with 2 mm sieve, washed with distilled water and modified with 1 M $FeCl_3$ solution and concentrated H_3PO_4 at 1:10 (w/v) and 1:5 (w/w) ratio respectively with 1 hour shaking and 24-hour contact period followed by filtration (**Zheng *et al*. 2022, Wu *et al*. 2017**). Following modification, the biochar was thoroughly washed, air dried, then oven dried at 60 ^{0}C for 8 hours, and finely grounded before mixing with soil.

Plant sample analysis and data calculation

Digestion of plant samples is done using di acid digestion mixture (HNO_3:$HClO_4$ :: 9:4) followed by volume was made up to 100 mL, filtered through Whatman 42 filter paper and reading was taken with atomic absorption spectroscopy (Agilent 240 FS-AA, USA). Percent reduction of metal concentration in any part of Rice is calculated by the following formula:

Comment [H1]: diacid

$$\% \text{ reduction} = [(X - Y) / X] \times 100$$

Where, X = Concentration of metal in respective part under control treatment (µg g^{-1}), Y = Concentration of metal in respective part under in the treatment concerned (µg g^{-1})

The diagrams are prepared using Microsoft excel.

Results and Discussion

Effect of biochar application in root heavy metal concentration

Heavy metal concentration in Rice roots has been considerably reduced after application of graded dose of biochar. A maximum of 26.71% reduction in Pb concentration in T10 has been reported followed by 26.28% in T7 (**Table 1**). Treatment T9 also performed better than other treatments. Least reduction of Pb concentration over control in root has been reported in T2 (**Figure 1**). Similarly, reduction of Cd (**Figure 3**) and Ni (**Figure 5**) accumulation over control is also reported to be lowest in T2 than other treatments. Treatment T4 and T6 performed similar results in reduction of Cd concentration over control plot in rice roots (**Table 1**). Performance of T9 is better than even T7 also (**Figure 3**). In case of Ni accumulation in roots, T7 and T10 has produced similar results in reduction of Ni accumulation in rice roots over control (**Figure 5**). Here, T6 performed better than T9 (**Table 1**). But in all the cases it is evident that application of modified biochar has performed better than simple biochar. **Zibaei et al. (2020)** outlined that after application of chitosan modified biochar, root and shoot accumulation of heavy metal was significantly reduced than the unmodified biochar. **Chatzimichailidou et al. (2023)** concluded that enhancement of surface area of biochar through modification process can better perform in absorbing arsenic from aqueous solutions. Phosphorus-rich materials, as indicated by **Xenidis et al. (2010)**, have the capacity to stabilize Cd and Pb in soils by creating insoluble metal-phosphate precipitates.

Effect of biochar application in reducing heavy metal concentration in stem

As compared to Cd and Ni reduction of Pb accumulation in Rice plant is more over the control plot (**Table 2**). This indicates transfer of lead from soil to plant has been much more affected by biochar application. **Peng et al. (2019)** reported that iron modified biochar derived from fruit shell significantly fixed Pb in soil (about 9.9%) in comparison with raw biochar treatment. Performance of T7 is also better than other treatments in reducing Pb accumulation in Rice stem (**Figure 1**). Treatments T4, T5 and T8 are almost similar in this respect. Lowest reduction of Cd concentration in Rice stem has been obtained in T2 followed by T8 and T5 respectively, where biochar was applied @ 5 t ha^{-1} (**Table 2**). Performance of T4, T6 and T10 is also almost similar in reducing Cd accumulation in Rice stem over control (**Figure 3**). However, modified biochar application has been proved to be better than simple biochar application in our study. **Irshad et al. (2022)** reported that goethite-modified biochar proved to reduce Cd uptake in Rice. Accumulation of Ni has also reduced after biochar administration. Despite lowest reduction of Ni accumulation in stem in T2, simple biochar at higher dose of 10 t ha^{-1} has proved to reduce it by 15.3% (**Figure 5**). A maximum of 21.2% reduction of Ni accumulation has been obtained under T7. **Yang et al. (2023)** demonstrated reduction of heavy metal accumulation in Rice after application of phosphorus enriched biochar by > 40%.

Effect of biochar application in reducing heavy metal concentration in grain

Transport of heavy metals from soil to plant depends on several factors. Root is considered as the first barrier of metal transport from soil to grain of Rice (**Qi *et al*., 2020**). Application of Fe-modified biochar @ 10 t ha-1 has diminished the Pb accumulation by 50% over control in our study. While, P-modified biochar reduced it by 45% (**Figure 2**). **Yang et al. (2023)** reported that application of P-enriched biochar has reduced Pb concentration of grain by 49.3%. However, application of modified biochar has performed better in reducing Pb accumulation in rice grain than simple biochar treatments depicted by similar performance of T4, T5 and T8 (**Table 4**). **Chatzimichailidou et al. (2023)** noted that presence of most promising functional groups in modified biochar is responsible for metal binding in soil rendering it unavailable for plants. Iron modified biochar performed better in reducing Cd concentration in Rice grain as well as in husk than simple or P-modified biochar (**Figure 4**). **Yoneyama et al. (2015)** depicted that Fe transport in Rice can alter Cd transport and accumulation of Cd in Rice grain. A maximum of 32.8% reduction of Cd concentration in grain was recorded in T7. **Ren et al. (2020)** indicated that phosphate modified biochar has reduced DTPA-extractable Cd in soil and its subsequent uptake in *Brassica rapa*. Maximum reduction of Ni in Rice grain has been obtained in T7 followed by T10 (**Figure 6**). However, performance of T4 and T8 are not much different indicating substitution of higher dose of simple biochar application with lower dose of modified biochar (**Table 4**). **Kumarathilaka et al. (2021)** observed that addition of iron-modified Si-rich biochar can be an effective strategy to reduce the concentrations of heavy metal in different rice tissues.

Comment [H2]: t ha^{-1}

Effect of biochar application in reducing heavy metal concentration in husk

Despite a 24.8% reduction in Pb concentration in Rice grain husk after application of simple biochar, Fe-modified biochar enhanced it almost twice (**Table 3**). Performance of T4, T5 and T8 are noted to be similar in reducing Pb concentration in Rice grain husk (**Figure 2**). Lowest reduction of Cd (**Figure 4**) and Ni (**Figure 6**) accumulation is noted in T2 followed by T3 and T5. There is practically no difference in performance of T9 and T10 in reducing husk Cd accumulation. While T7 followed by T10 shows highest diminution of Ni accumulation in husk over control treatment (**Figure 6**). **Liu et al. (2020)** showed that biochar incorporation can effectively reduce Cd accumulation below the safe limits in alfalfas. **Ahmad et al. (2018)** indicated that P-loaded biochar application not only enhanced maize growth and yield but also reduced heavy metals uptake by immobilizing them in soil. **Khan et al. (2020)** outlined that biochar application can reduce the human health risk associated with heavy metals toxicity in Rice by immobilizing them in a heavily contaminated mine soil.

Conclusion

Our study reveals that biochar application in a metal contaminated soil can effectively reduce metal accumulation in different parts of Rice (root, stem, husk and grain). However, metal accumulation in grain, husk and stem can vary for different metals; might be due to their different behaviour in plant body. Modification of biochar is helpful not only in reducing metal accumulation but also cutting off application dose as compared to simple biochar. Thus, biochar application can be a promising strategy to mitigate metal contaminated soil.

Comment [H3]: behavior

Comment [H4R3]:

Comment [H5R3]:

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Table 1: Percentage reduction of Pb, Cd and Ni concentration over control in roots of Rice with graded dose of biochar

Treatment	Pb	Cd	Ni
T2	5.34	9.32	3.07
T3	9.55	11.50	7.14
T4	10.47	19.82	15.97
T5	8.97	13.84	14.59
T6	14.10	19.94	18.96
T7	26.28	22.23	20.84
T8	13.25	15.50	13.34
T9	20.94	23.46	16.06
T10	26.71	26.80	20.32

Comment [H6]: Pls add one more column after **Treatment** for short explanation or each treatment!

Comment [H7R6]:

Table 2: Percentage reduction of Pb, Cd and Ni concentration over control in stem of Rice with graded dose of biochar

Treatment	Pb	Cd	Ni
T2	25.22	6.04	3.54
T3	30.27	11.28	6.65
T4	32.83	17.37	15.29
T5	32.97	9.74	12.36
T6	39.06	18.79	16.85
T7	44.89	20.87	21.20
T8	33.64	8.87	11.08
T9	40.97	15.90	13.87
T10	49.61	17.00	18.24

Comment [H8]: Pls add one more column after **Treatment** for short explanation or each treatment!

Table 3: Percentage reduction of Pb, Cd and Ni concentration over control in husk of Rice with graded dose of biochar

Treatment	Pb	Cd	Ni
T2	24.79	8.05	4.78
T3	30.40	14.16	7.19
T4	32.01	18.54	11.67
T5	32.86	13.03	10.40
T6	38.66	17.60	14.12
T7	44.06	23.76	20.97
T8	32.77	23.67	9.39
T9	41.25	28.73	14.29
T10	48.66	28.90	17.65

Table 4: Percentage reduction of Pb, Cd and Ni concentration over control in grain of Rice with graded dose of biochar

Treatment	Pb	Cd	Ni
T2	25.31	15.41	17.85
T3	30.95	20.51	27.31
T4	32.69	25.56	33.76
T5	33.22	21.47	24.19
T6	39.03	28.16	37.96
T7	44.97	32.84	50.32
T8	33.80	24.34	31.29
T9	42.70	30.02	40.65
T10	50.26	31.77	48.17

x

Comment [H9]: Pls add one more column after **Treatment** for short explanation or each treatment!

Comment [H10]: Pls add one more column after **Treatment** for short explanation or each treatment!

Comment [H11]: Pls put standard error bar in all figures!

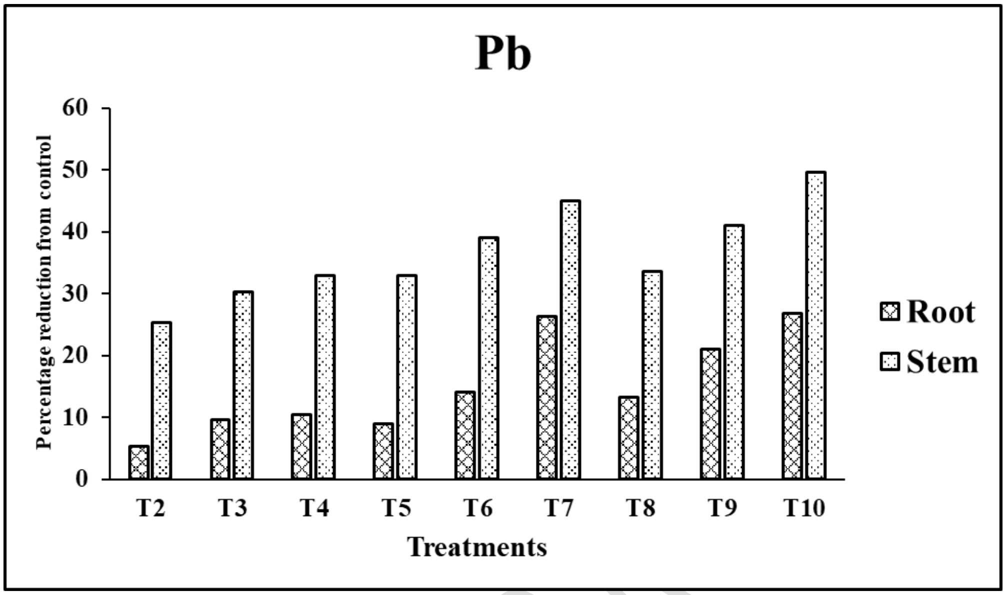

Figure 1: Percentage reduction of Pb accumulation over control in root and stem of Rice under varying biochar treatments in metal contaminated soil

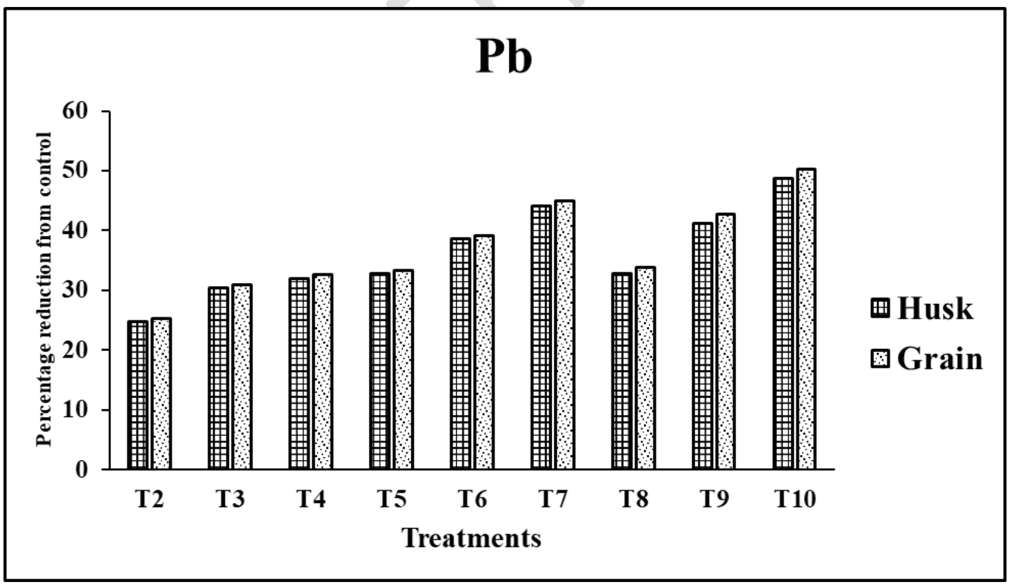

Figure 2: Percentage reduction of Pb accumulation over control in husk and grain of Rice under varying biochar treatments in metal contaminated soil

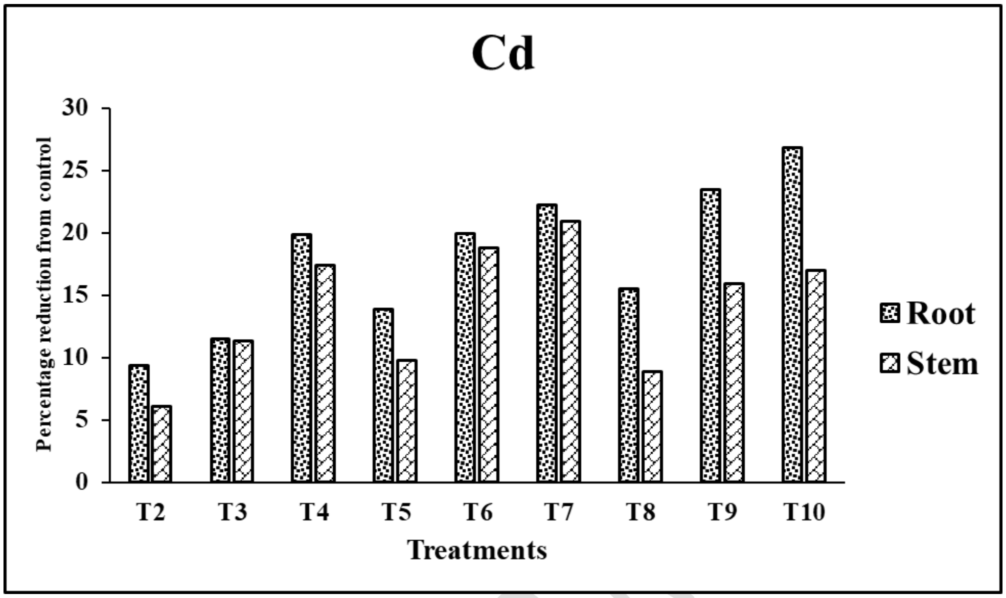

Figure 3: Percentage reduction of Cd accumulation over control in root and stem of Rice under varying biochar treatments in metal contaminated soil

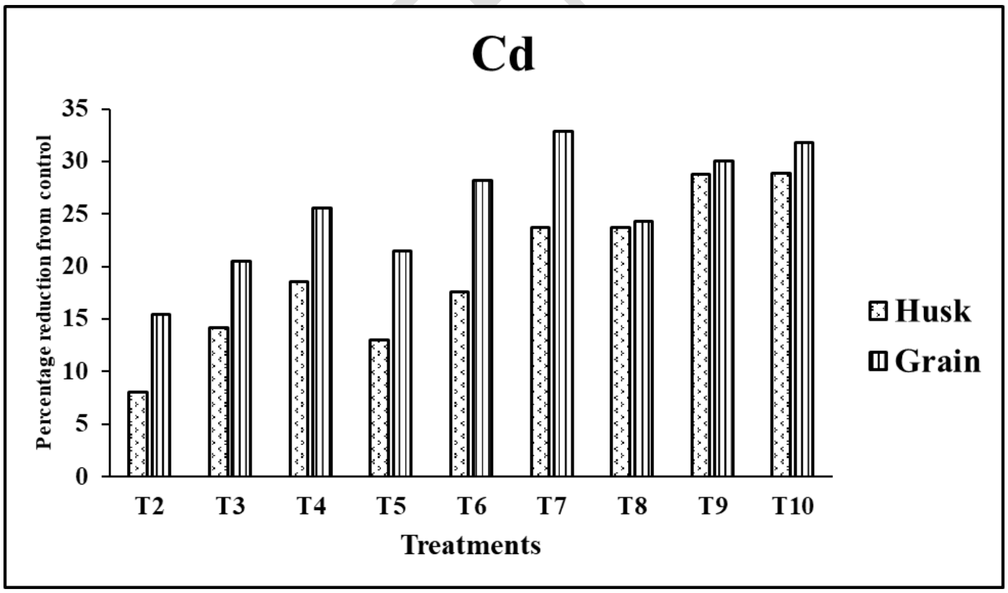

Figure 4: Percentage reduction of Cd accumulation over control in husk and grain of Rice under varying biochar treatments in metal contaminated soil

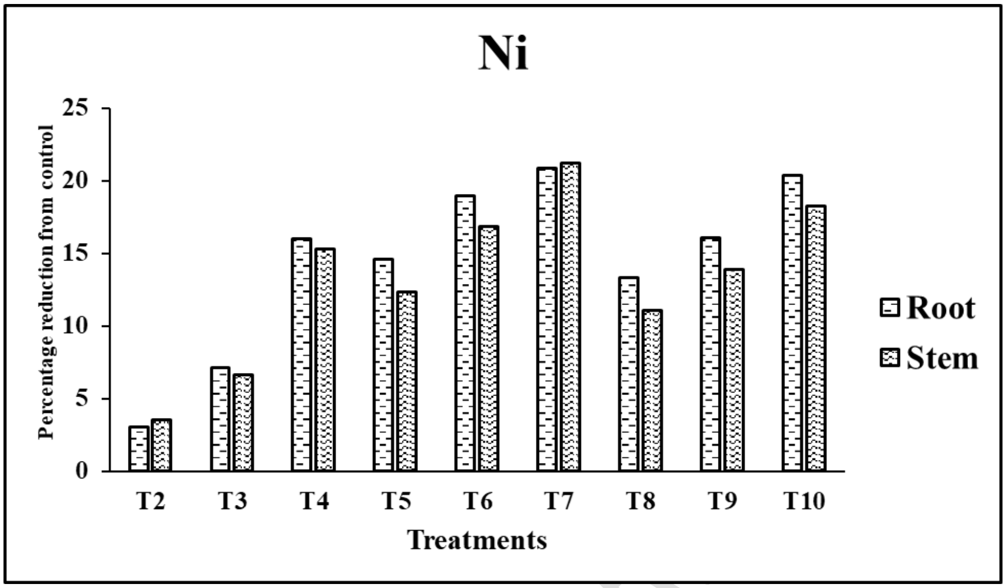

Figure 5: Percentage reduction of Ni accumulation over control in root and stem of Rice under varying biochar treatments in metal contaminated soil

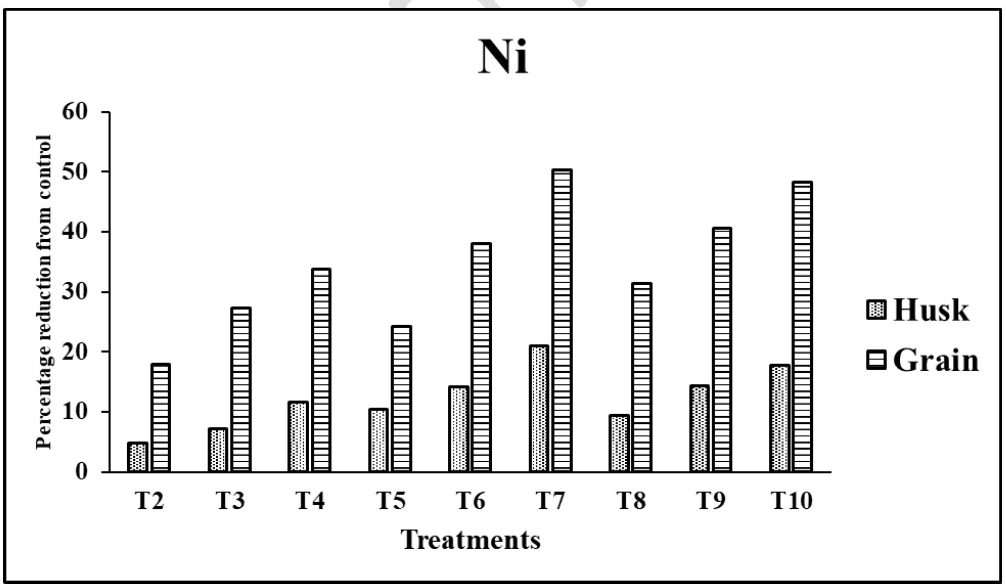

Figure 6: Percentage reduction of Ni accumulation over control in husk and grain of Rice under varying biochar treatments in metal contaminated soil