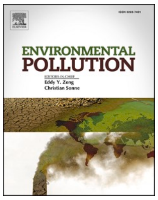
Environmental Pollution 309 (2022) 119733

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol



In-situ stabilization of potentially toxic elements in two industrial polluted soils ameliorated with rock phosphate-modified biochars☆

Tanveer Hussain [a], Samreen Riaz Ahmed [b], Altaf Hussain Lahori [a,*], Monika Mierzwa-Hersztek [c], Viola Vambol [d,e], Asif Ali Khan [a], Lubna Rafique [a], Sajid Wasia [a], Muhammad Faizan Shahid [a], Zhang Zengqiang [f]

[a] Department of Environmental Sciences, Sindh Madressatul Islam University, Karachi, 74000, Pakistan
[b] Department of English, Sindh Madressatul Islam University, Karachi, 74000, Pakistan
[c] Department of Agricultural and Environmental Chemistry, University of Agriculture in Krakow, al. Mickiewicza 21, 31-120, Krakow, Poland
[d] Department of Environmental Engineering and Geodesy, University of Life Sciences in Lublin, Lublin, Poland
[e] Department of Applied Ecology and Environmental Sciences, National University «Yuri Kondratyuk Poltava Polytechnic», Poltava, Ukraine
[f] College of Natural Resources and Environment, Northwest A & F University, Yangling, Shaanxi, 712100, China

ARTICLE INFO

Keywords:
Immobilization
Mustard
Potentially toxic elements
Rock phosphate-modified biochars
Biomass growth

ABSTRACT

The present study was aimed at determining the efficacy of rock phosphate (RP) 3% loaded in a green coconut shell, chicken manure, and vegetable waste to make green coconut-modified biochar (GMB), chicken manure modified-biochar (CMB), and vegetable waste-modified biochar (VMB) in the fixation of Cr, Pb, Cu, Zn, Ni, and Cd in Sharafi goth and Malir polluted soils. The impact of RP impregnated with organic waste material to produce modified biochars (MBs) on stabilizing PTEs from polluted soils and reducing their uptake by mustard plant has not yet been thoroughly investigated. All modified BCs in 0.5, 1, and 2% doses were used to stabilize Cr, Pb, Cu, Zn, Ni, and Cd in two polluted soils and to reduce their uptake by the mustard plant. The obtained results revealed that the maximum mustard fresh biomass was 17.8% higher with GMB 1% in Sharafi goth polluted soil and 25% higher with VMB 0.5% in Malir polluted soil than in the control treatment. After applying modified BCs, immobilization of Cr, Pb, Cu, Ni, and Cd was observed in both soils and it reduced the uptake of these elements by mustard plants. On the other hand, although Zn mobilization increased by 0.38% for CMB 0.5% and by 5.9% for VMB 0.5% in Sharafi goth polluted soil, as well as by 3.15% for GMB 1%, 6.34% for GMB 2%, and 4.78% for VMB 0.5% in Malir polluted soil, this was due to changes in soil pH and OM. It was found that GMB 1%, CMB 0.5%, and VMB 0.5% have the potential to increase Zn uptake by mustard, while VMB 2% can reduce the element uptake by the plant. Redundancy analysis showed that soil chemical parameters were negatively correlated with PTEs in both soils and reduced their uptake by mustard. The present study revealed that MBs can stabilize PTEs in industrial and wastewater soils polluted with multiple metals and reduce their uptake by plants.

1. Introduction

Soil pollution with potentially toxic elements (PTEs) is considered one of the most severe ecological threats, while among reclamation approaches, investigation of soil additives has received significant attention (Wang et al., 2018; Rajendran et al., 2022). Excessive accumulation of PTEs such as Cr, Pb, Cu, Zn, Ni, and Cd in the soil is a global challenge due to geogenic and anthropogenic processes (Rinklebe and Shaheen, 2015; Palansooriya et al., 2020). Remediation of polluted soils is imperative to ensure safer crop production (A. H. Lahori et al., 2020). Soil PTEs are considered the most polluting elements in soil, and their basic characteristics are non-degradability, perseverance, and bioaccumulation in the food web (Gholami et al., 2020). Nearly 12.6 million people have died worldwide in recent years from more than 100 diseases caused by unhealthy ecosystems, such as polluted soils (WHO, 2016). Soil pollution with PTEs leads to land degradation or loss of some soil functions on a global scale (Puga et al., 2015).

PTEs are released into the environment through atmospheric deposition from industrial effluent, dumping, mining, smelting, pesticides,

---

☆ This paper has been recommended for acceptance by Dr Montes Marques.
* Corresponding author.
E-mail address: altaf@smiu.edu.pk (A.H. Lahori).

https://doi.org/10.1016/j.envpol.2022.119733
Received 14 May 2022; Received in revised form 3 July 2022; Accepted 4 July 2022

List of abbreviations

PTEs	Potentially toxic elements
RP	Rock phosphate
GMB	Green coconut-modified biochar
CMB	Chicken manure-modified biochar
VMB	Vegetable waste-modified biochar
BCs	Biochars
MBs	Modified biochars
MLA	Malir industrial area
SGK	Sharafi goth korangi

sewage sludge, electric waste, commercial fertilizers, etc. (Qiao et al., 2020). There are more than 6000 different industrial plants in Karachi including refineries, chemical plants, petrochemical plants, tanneries, textile plants, pharmaceutical plants, solid waste and sewage sludge treatment plants, etc. All of them produce large amounts of effluent that is highly contaminated by organic and inorganic pollutants, which are also responsible for a significant degree of soil contamination (Afzal et al., 2018). Excessive accumulation of PTEs in soil leads to land degradation and retards crop production and requires remediation using environmentally friendly, feasible, and low-cost techniques (Derakhshan-Nejad and Jung, 2017). At the same time, PTE pollution in the food chain is a serious problem that threatens living organisms (Antoniadis et al., 2017). The mobility and adsorption of PTEs in soils are strongly influenced by the chemical fractionation of elements in the polluted soil (Chao et al., 2018). Numerous in-situ and ex-situ soil reclamation/restoration technologies have been used to reduce the risk of pollution with PTEs and exploit arable land for agricultural purposes to ensure food security (Wang et al., 2015; Beiyuan et al., 2017a,b). In-situ technologies viz., solidification/stabilization (Li et al., 2018), soil washing/flushing (Beiyuan et al., 2018), bioremediation (Park et al., 2011), and ex-situ techniques such as soil washing (Beiyuan et al., 2017a,b), vitrification landfilling, and bioreactors are often used to diminish bioavailability of PTE pollutants (Kuppusamy et al., 2016). With the growing threat to human health posed by polluted soils, the identification and optimization of soil restoration technologies are becoming increasingly important. All these soil restoration technologies have dissimilar overall working values and specific merits and demerits. In addition, technology potential and cost-effectiveness can vary drastically between in-situ and ex-situ trials (Khalid et al., 2017). Among these techniques, the application of soil additives to stabilize PTEs has been extensively employed to restore PTE-polluted soils; this results from its rapid and easy incorporation as well as commercial feasibility (Beiyuan et al., 2016). Choosing the appropriate stabilizers can deliver cost-effective restoration methods and fulfill the "green and sustainable remediation" assumption due to their lower life cycle ecological footprint (Hou and Al-Tabbaa, 2014).

Certainly, rock phosphate (RP) is the primary source of P that can be used to manufacture single superphosphate (SSP) or triple superphosphate (TSP) fertilizer in Pakistan to improve soil health and crop production (Lahori et al., 2019). Involvement in the production of phosphate raw materials with a P_2O_5 content less than 24% is not economically feasible. The dominant phosphate reserves are located in Khyber Pakhtunkhwa and Hazara divisions in the northeastern part of the country; unfortunately, there are no consistent skills to make it suitable for local alkaline soils. The soils of Pakistan are alluvial, with $CaCO_3 > 3.0\%$ and no native P. Indeed, RP is a natural, inexpensive, and clean complex material, but, unfortunately, has a low P content and its solubility is too slow to meet the plant demand and stabilize pollutants. As many as 90% of soils in Pakistan are already deficient in P. Direct application of RP to acidic soil may solubility the P content, whereas its solubility may be impaired in alkaline and/or calcareous soils due to high pH and low organic matter content (Ishtiaq and Ahmad, 1987; Rahman et al., 2018). It can be assumed that mixing PR with organic waste material to produce modified BCs can be highly effective in stabilizing PTEs in multi-metal-polluted soil and reduce metal uptake by plant, as PR has a high potential to adsorb pollutants in the soil medium (Caravaca et al., 2004). Biochar (BC) as an amendment originated in Terra Preta Soils (Glaser et al., 2002). In the last few years, BC has been broadly studied and applied as an efficient soil development and remediation material (Downie et al., 2009; Ahmad et al., 2017). BC is a solid and C-rich product formed by heating feedstock under O_2-limited conditions (Cao and Harris, 2010). Generally, BC is pyrolyzed at low and high temperatures from agricultural/forestry waste, fruit waste, algae, tire waste, dead animals, food waste, and livestock manure as a feedstock for PTE remediation in polluted soils (Novak et al., 2013; Gul et al., 2015). Several studies have shown that the BC can reduce the bioavailability of PTEs in soil by increasing soil pH, cation exchange capacity, carboxyl groups, hydroxide ion complexation, etc. (Lahori et al., 2017; Igalavithana et al., 2017). Some researchers have found that BC can increase nitrogen (N) content, water holding capacity, nutrient retention, microbial activity, soil fertility and productivity (Houben et al., 2013; Puga et al., 2015). Over the past few years, modified biochar (MBC) has been successfully used to stabilize PTEs in polluted soils. A study by Ren et al. (2020) assessed the potential of $Ca(H_2PO_4)_2$-based pig manure biochar to bind Cd and Pb in smelter-polluted soils. Furthermore, Gholami et al. (2020) examined the efficacy of thiourea-modified BC in the stabilization and speciation of Cd and Pb in acidic polluted soil. Additionally, Irshad et al. (2020) investigated the potential of goethite-modified biochar to fix Cd and As in contaminated soil and promote the growth of rice. Zhang et al. (2020) applied phosphorus-modified biochars to stabilize Cu, Cd, and As in contaminated paddy soil. What is more, Wang et al. (2021) reported that Fe/Mn- and P-modified drinking water treatment residuals can decrease Cu and Pb concentrations in mining-polluted soil and reduce their uptake by ryegrass. From a novel point of view, limited information is available on the activation of 3% rock phosphate impregnated with green coconut shell, chicken manure, and vegetable waste biomass to make modified biochars (MBs) pyrolyzed at <500 °C to stabilize Cr, Pb, Cu, Zn, Ni, and Cd in industrial soils polluted with multiple metals and reduce their absorption by mustard plants. Therefore, the main objectives of the present study were: 1) to explore the impact of rock phosphate loaded 3% in green coconut shell, chicken manure, and vegetable waste to make green shell-modified biochar (GMB), chicken manure-modified biochar (CMB), and vegetable waste-modified biochar (VMB) on the fixation of Cr, Pb, Cu, Zn, Ni, and Cd in Sharafi goth and Malir polluted soils; 2) to investigate the effect of different concentrations of modified biochars on the phytoavailabilty of Cr, Pb, Cu, Zn, Ni, and Cd to the mustard plant; and 3) to assess the impact of different rock phosphate-modified biochars on soil chemistry. It was hypothesized that different rock phosphate-modified biochars can immobilize multi-toxic elements in industrial and wastewater polluted soils and reduce their uptake by plants.

2. Material and methods

2.1. Soil collection and characterization

In the present study, two different soils samples were collected from Malir Industrial Area (MLA) (24°51′38 ″N; 67°13′30 ″E), Sharafi goth Korangi (SGK) (24°.85′76 ″N; 67°.16′76″E) Sindh Province, Pakistan (Fig. S1). Surface soil samples were collected from 0 to 15 cm layer from Sharafi goth and Malir areas. Composite soil samples were taken from different points. The soil samples were air-dried for 1 week. Debris and non-soil material were separated manually, and soil samples were <2 mm ground. Selected basic physicochemical parameters of both soils are given in (Table 1).

Table 1
Physico-chemical characteristics of the studied soil and its amendments.

Parameters	SGPS	MPS	RP	GMB	CMB	VMB
Soil texture	Sandy loam	Sandy clay loam	-	-	-	-
pH	6.99 ± 0.7	6.92 ± 0.2	7.80 ± 0.8	7.95 ± 0.7	8.44 ± 0.4	10.6 ± 0.6
EC (mS/cm)	2.37 ± 1.2	2.05 ± 0.6	0.9 ± 0.2	27.6 ± 1.2	42.3 ± 0.5	66.6 ± 0.1
SOC (g/kg)	40.9 ± 0.3	40.1 ± 1.2	–	49.9 ± 1.8	55.3 ± 0.2	66.53 ± 0.2
Organic matter (g/kg)	70.6 ± 1.2	69.3 ± 0.7	–	86.1 ± 0.9	96.08 ± 0.8	100.2 ± 0.6
Pb (mg/kg)	70.7 ± 1.6	143.6 ± 0.9	–	–	–	–
Cd (mg/kg)	8.3 ± 0.6	11.4 ± 1.5	–	–	–	–
Zn (mg/kg)	470.1 ± 0.5	483.8 ± 1.1	–	–	–	–
Cu (mg/kg)	38.9 ± 1.2	46.6 ± 0.7	–	–	–	–
Cr (mg/kg)	239.8 ± 1.5	246.9 ± 1.4	–	–	–	–
Ni (mg/kg)	9.9 ± 0.5	15.3 ± 0.7	–	–	–	–
Biochar yield (g/100 g dry matter)	–	–	–	37.8 ± 0.6	51.02 ± 0.8	33.4 ± 0.3

SGPS: Sharafi Goth polluted soil.
MPS: Malir polluted soil.
RP: Rock phosphate
GMB: Green coconut shell-modified biochar
CMB: Chicken manure-modified biochar
VMB: Vegetable waste-modified biochar

2.2. Material collection and modified biochar preparation

Rock phosphate (RP) was obtained from Kakul Mine Haripur Hazara areas of Khyber Pakhtunkhwa (34°.10′05″N; 73°.13'.28″E). Green coconut shell was collected at the local market, chicken manure came from chicken farms, and vegetable waste was collected at the vegetable market in Karachi, Pakistan. In the first step, to prepare modified BCs, dry feedstocks, i.e. green coconut shell, chicken manure, and vegetable waste, were ground and 2 mm sieved, and then <1 mm sieved dry rock phosphate (RP) was carefully mixed with individual feedstocks. In the second step, all the mixed material was placed in a muffle furnace and pyrolyzed at <500 °C for 3 h to produce green coconut-modified biochar (GMB), chicken manure-modified biochar (CMB), and vegetable waste-modified biochar (VMB). Except for the control treatment, all three MBs were added to both soils in 0.5, 1, and 2% doses.

2.3. Experimental set-up

The efficacy of modified biochars in the phytoextraction of Ni, Cr, Pb, Cu, Zn, and Cd by mustard (*Brassica napus*) was investigated on Sharifi goth and Malir polluted soils in a greenhouse pot experiment. Immobilizing agents such as green coconut-modified biochar (GMB), chicken manure-modified biochar (CMB), and vegetable waste-modified biochar (VMB) were applied in doses of 0.5, 1, and 2% (*w/w*) (Ali et al., 2019). In addition, all modified biochars were ground, <2 mm sieved, and carefully mixed with polluted soils, except for the control soil samples. Approximately 1.0 kg of each air-dried sample together with 0.5, 1, and 2% doses (*dry matter/weight*) of each modified BC were placed in 38 cm diameter pots to cover each pot to a height of 12 cm. All treatments were applied to polluted soils in three replicates – randomized complete block design (RCBD). This design included 60 pots (2 soils × 10 treatments × 3 replicates and 1 crop). Soils and each modified BC were thoroughly mixed and placed in pots for investigation. All pots were irrigated with almost 300 ml of tap water to achieve a moisture content of approximately ~65% of the soil moisture content. All pots were incubated for 15 days for chemical reaction. Furthermore, mustard seeds were treated with a suspension of H_2O_2 (3%, *v/v*) for 15 min and then washed with pure water about 3 times. About 5 to 7 seeds were sown in each pot and after 10–15 days, reduced to 3 plants per pot. At the time of mustard sowing, the field capacity was adjusted to nearly 80%. Water losses in each pot were replenished daily. All mustard plants were harvested within 50 days.

2.4. Sample analysis

2.4.1. Soil and modified biochar analyzes

All chemical solutions were prepared using deionized water, and all chemicals used in our study were of pre-analytical grade. The EC and pH were measured using deionized water (1:5 H_2O ratio) in both soil samples, rock phosphate, and modified biochars, respectively. The SOC content in soils and modified BCs was determined using elemental analysis (Mebius, 1960). The total lead, cadmium, copper, chromium, zinc, and nickel contents in modified BCs were tested by the United States Environmental Protection Agency method 3050 B (The United States Environmental Protection Agency, 1996). The surface functional groups of all three modified BCs were characterized by Fourier transform infrared (FTIR) spectroscopy with the use of a Bruker Vector 22 FTIR spectrophotometer in the range of 4000–400 cm^{-1}. The samples were mixed with KBr powder (1%, w/w) until homogenized and pressed by applying mechanical pressure to form a KBr disk (Fig S2).

2.4.2. Mustard plant analysis

Mustard plants were harvested about fifty days after planting. All plants were carefully uprooted, washed, and then placed in paper bags to determine total biomass (shoots and roots) and for further chemical analyzes. The dry matter of plant biomass (shoots and roots) was recorded after drying at 65 °C for 3–4 days. The dried plant biomass was then crushed in a small electric machine to obtain powder, after which the crushed dry biomasses of roots and shoots were stored in paper bags for testing. Almost 0.5 g of HNO3 − HClO4 mixture in a 4:1 ratio was used according to Lindsay (1978) to determine the contents of nickel, copper, lead, chromium, cadmium, and zinc in plant roots/shoots. The total contents of these elements in the treated samples were detected by digesting 0.2 g of soil in a mixed solution of HF–HClO4– HNO3– Zhu et al. (2018). The proportions of PTEs in the dissolved samples were detected by AAS instrument using the United States Environmental Protection Agency method 3050 B (The United States Environmental Protection Agency, 1996).

2.5. Statistical analysis and quality control

All trial data were statistically analyzed using Statistix 8.1. The mean of 3 replicates was subjected to the HSD test at $p < 0.05$. OriginPro 16 software was used to prepare the graphs. RDA analysis was performed in CANOCO 5 to determine the correlation between soil toxic metals, plant growth, toxic metals in plant roots and shoots, and soil chemical properties. Certified reference materials for soil GBW07457 (GSS-28) and plant GBW07603 (GSV-2 mustard) according to the Chinese Academy of Geological Sciences were used for quality control. The recovery rates of Pb, Cu, Zn, Ni, and Cd in soil were 93–101, 94–103, 95–102, 91–101, and 94–103%, respectively, and in plant 91–104, 93–102, 92–104, 90–101, and 93–105%, respectively.

3. Results and discussion

3.1. Properties of studied soils and additives

The properties of Sharafi goth and Malir soils are shown in (Table 1). Soil pH was nearly neutral (6.99 and 6.92) and the organic matter content was higher (70.12 g/kg and 69 g/kg), with moderate EC (2.37

and 2.05 mS/cm, respectively). The total concentration of PTEs was compared with standards (Denneman and Robberse, 1990; WHO, 1996). All the PTEs tested exceeded the limits of the WHO standard, with the exception of Ni, and were therefore compared with the standard value of 35 mg/kg in the studied experiment. The physiochemical results revealed that both soils were highly polluted with PTEs. In addition, the texture of Malir polluted soil was sandy clay loam, while in the case of Sharafi goth it was sandy loam (Table 1). The GMB and CMB additives had slightly neutral pH, while VMB was alkaline. The pH values of the additives were: 7.95 for GMB, 8.44 for CMB, and 10.6 for VMB. The electrical conductivity values were 27.6 mS/cm (GMB), 42.3 mS/cm (CMB), and 66.6 mS/cm (VMB). The soil organic carbon content was the highest in VMB (66.6 g/kg), followed by VMB (55.34 g/kg) and GMB (49.9 g/kg). The highest organic matter content was found in VMB (100.2 g/kg), followed by CMB (96.08 g/kg) and then GMB (49.9 g/kg). In terms of biochar yield, the most biochar was produced from CMB (51.02%), followed by GMB (37.8%), and the least from VMB (33.40%).

3.2. *FTIR results of modified biochars*

The Fourier transform infrared (FT-IR) spectrum of biochar pyrolyzed from GMB, CMB, and VMB is illustrated in (Fig. S2). FTIR analysis was performed to evaluate the chemical components or functional groups present in the biochar, which are responsible for the stabilization of PTEs in contaminated soil. The red trace FTIR spectra revealed the presence of CMB, which showed a peak at 3450 cm^{-1} and 2922 cm^{-1}, corresponding to the O–H and C–H stretching frequencies, respectively. The peak that appeared at 1641 cm^{-1} indicated the carbonyl ($C{=}O$) of amide, while the peak at 1424 cm^{-1} revealed the bending frequency of N–H of the secondary amide. The medium intense peak at 1093 cm^{-1} indicated the presence of a C–O bond in the system. The black trace FTIR spectra showed the major peaks in the GMB biochar. The broad peak at

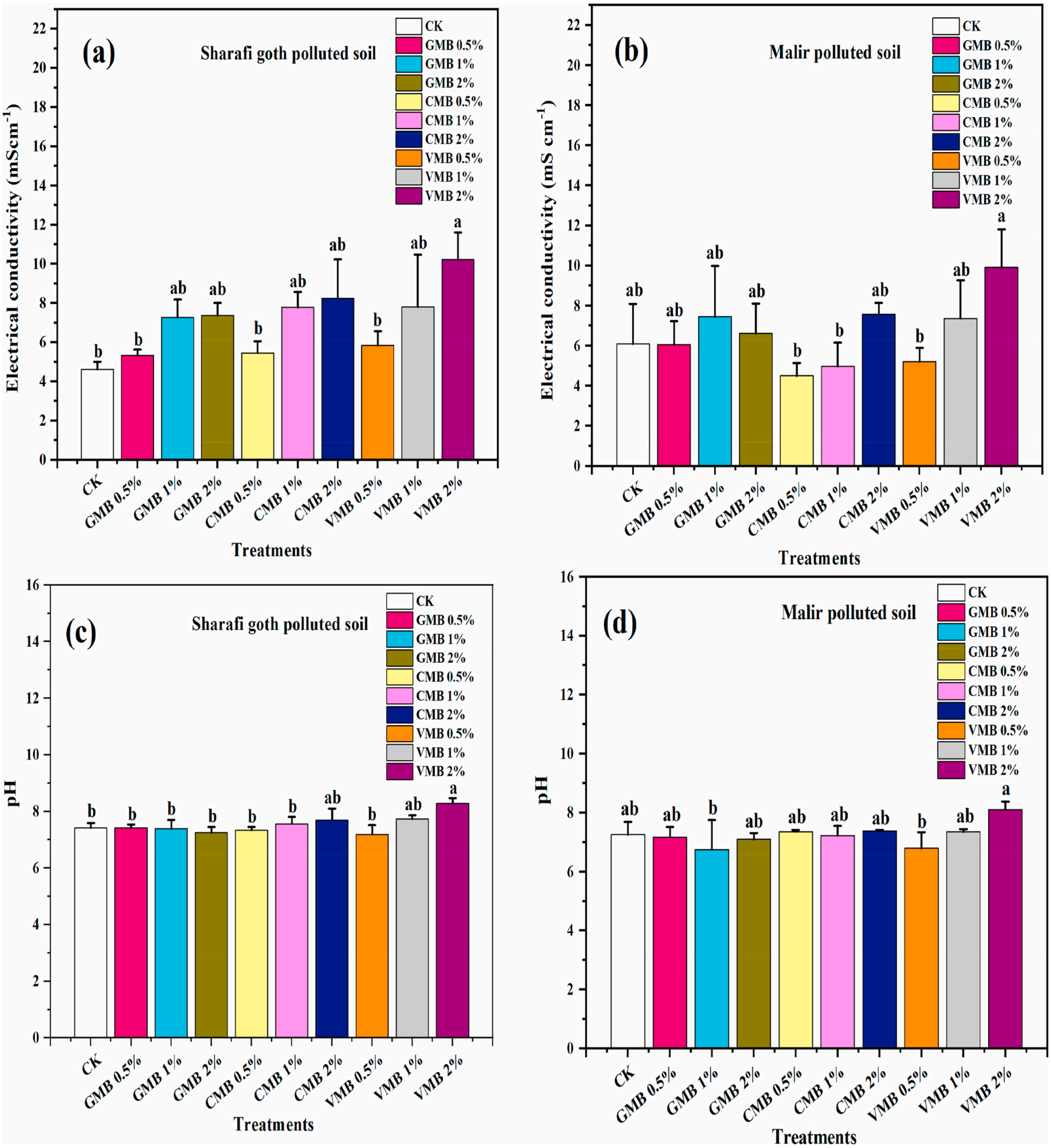


Fig. 1. Impact of modified biochars on: electrical conductivity in Sharafi goth polluted soil (a) and Malir polluted soil (b); pH in Sharafi Goth polluted soil (c) and Malir polluted soil (d).

3438 cm^{-1} of high intensity corresponded to the presence of O–H stretching vibrations with high hydrogen bonds and the N–H group. On the other hand, the absorption peak at 2923 cm^{-1} indicated the presence of asymmetric C–H stretching frequency. The peak at 1593 cm^{-1} was attributed to the vibration (C = C) and the peak at 1384 cm^{-1} to bending vibrations of $-CH_3$ and the C–N group. The peak at 1259 cm^{-1} corresponded to C–O stretching vibrations; finally, the peak at 671 cm^{-1} was attributed to C–H stretching vibrations and/or halogen trace as previously indicated in the literature (Alshehri et al., 2014). The blue trace FTIR spectra revealed the major peaks in the VMB biochar. The broad peak at 3550 to 3377 cm^{-1} corresponded to the presence of O–H stretching vibrations with hydrogen bonds and the N–H group. On the other hand, the absorption peak at 2923 cm^{-1} indicated the presence of asymmetric C–H stretching frequency. The absorption peak that appeared at 1741 cm^{-1} was attributed to the vibration (C = O) and the peak at 1399 cm^{-1} to bending vibrations of –N-H and the C–N group. The peak at 1040 cm^{-1} corresponded to C–O stretching vibrations, while the peak at 671 cm^{-1} was attributed to halogen and/or C–H stretching vibrations of the aliphatic alkane (Fig. S2).

3.3. *Effect of amendments on soil EC and pH*

After harvesting mustard (*Brassica juncea* L) from pots, the impact of modified BCs on soil EC and pH were investigated in Sharafi goth and Malir polluted soils. All modified BCs significantly increased EC in Sharafi goth polluted soil, while for Malir polluted soil more diversified parameter changes were observed. The maximum EC in Sharafi goth polluted soil ranged from 4.62 to 10.22 mS/cm with the application of VBC 2% (Fig. 1a). In Malir polluted soil, the highest EC was between 6.10 and 9.91 mS/cm with the addition of VMB 2%, while the lowest EC ranged from 6.10 to 4.50 mS/cm with the application of CMB 0.5% compared to the control (Fig. 1b). The addition of BC ash into the polluted soil increased the EC of soil (Kolton et al., 2011). Ali et al. (2019) reported that EC and pH in mining soil increased after applying wood BC to it. The addition of biochars significantly increased electrical conductivity in calcareous soil Karimi et al. (2020).

Changes in pH levels were observed in Sharafi goth and Malir polluted soils. Compared to the control treatment, the highest pH level in Sharafi goth polluted soil ranged from 7.41 to 8.28 with the

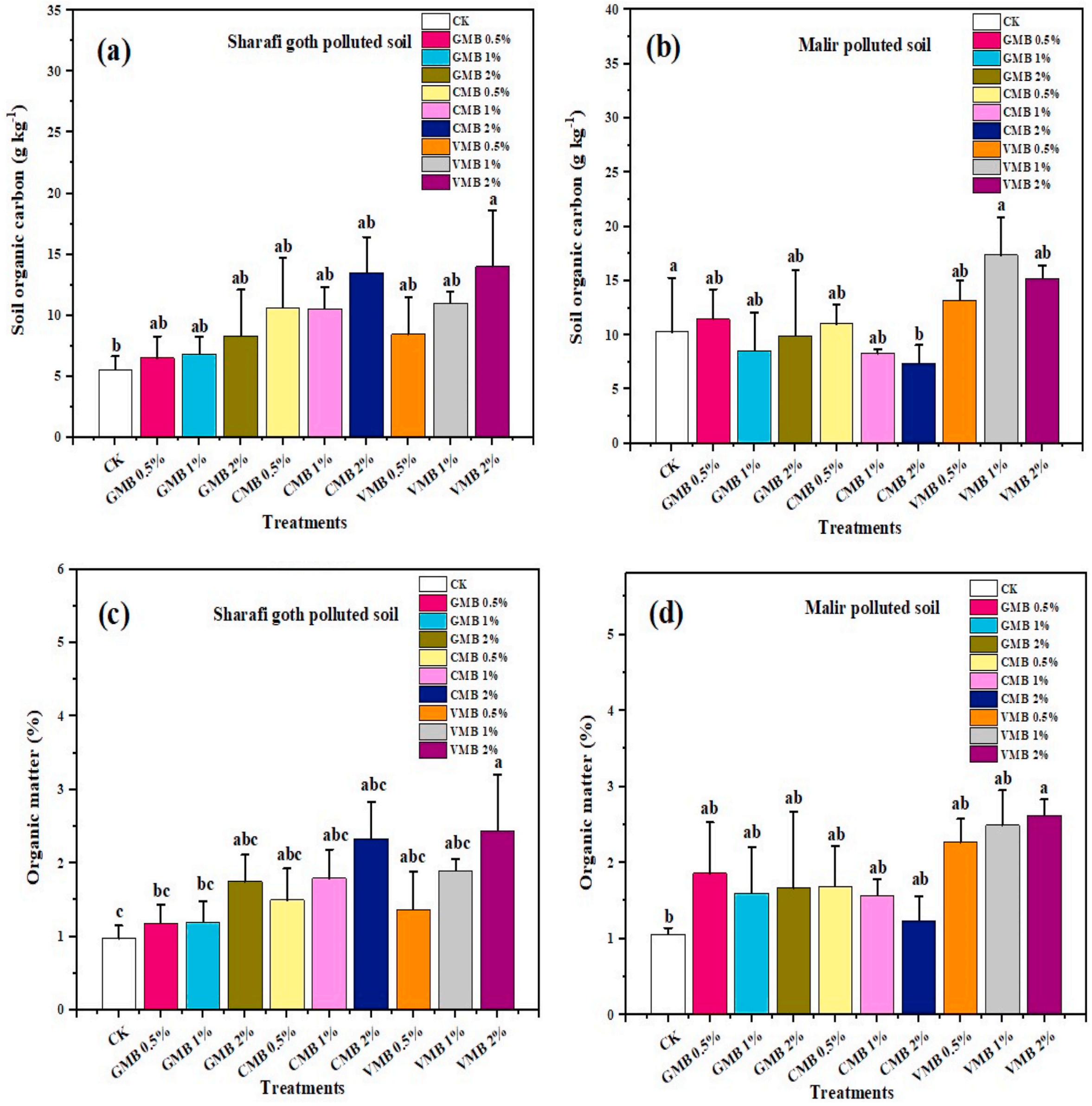


Fig. 2. Impact of modified biochars on: soil organic carbon in Sharafi Goth polluted soil (a) and Malir polluted soil (b); organic matter in Sharafi goth polluted soil (c) and Malir polluted soil (d).

application of VMB 2%, and the lowest pH level was between 7.41 and 7.19 following the addition of VMB 0.5% (Fig. 1c). The application of modified BCs caused changes in Malir polluted soil. The highest pH value significantly increased and ranged from 7.26 to 8.11, with the highest value reported after the application of VMB 2%. The lowest pH value was significantly reduced from 7.26 to 7.10 with the application of GMB 2% compared to the control soil (Fig. 1d). It should be noted that pH is the key factor through which biochars interact with pollutants (Ahmad et al., 2014). Higher metal removal efficiency with increasing BC application rate was attributed to an increase in pH (Xu et al., 2013; Komkiene and Baltrenaite, 2016). According to Berihun et al., 2017), soil pH can be improved by applying BC, by comparing it with the control samples of soil amendment. Zhang et al. (2019) stated that the application of BC and fertilizer can cause minor variation in soil pH. The application of BC in soil has the potential to increase soil pH, which can be considered one of the key factors for stabilizing PTEs in polluted soil (Taskin et al., 2019).

3.4. *Effect of amendments on soil SOC and OM*

All modified biochars were able to significantly increase the soil organic carbon (SOC) in Sharafi goth polluted soil as compared with control. The highest SOC observed in Sharafi goth polluted soil was 60.50% after applying VMB 2% (Fig. 2a). Changes in SOC were observed in Malir polluted soil after harvesting mustard plants grown with modified biochars. The maximum concentration of SOC in Malir polluted soil reached 40.8% after applying VMB 1%, while CMB 2% reduced the SOC content to 28.08% as compared with control (Fig. 2b). All modified biochars were found to be highly effective in increasing soil organic matter (OM) in Sharafi goth and Malir polluted soils. The maximum OM content in Sharafi goth and Malir soils was 60.24% and 59.6%, respectively, with the application of VMB 2% as compared with control (Fig. 2c and d). Karimi et al. (2020) reported that the application of BCs enhanced SOC in alkaline calcareous soil.

3.5. *Impact of soil amendments on fresh and dry biomass yield*

The growth of mustard plant in Sharafi goth and Malir polluted soils

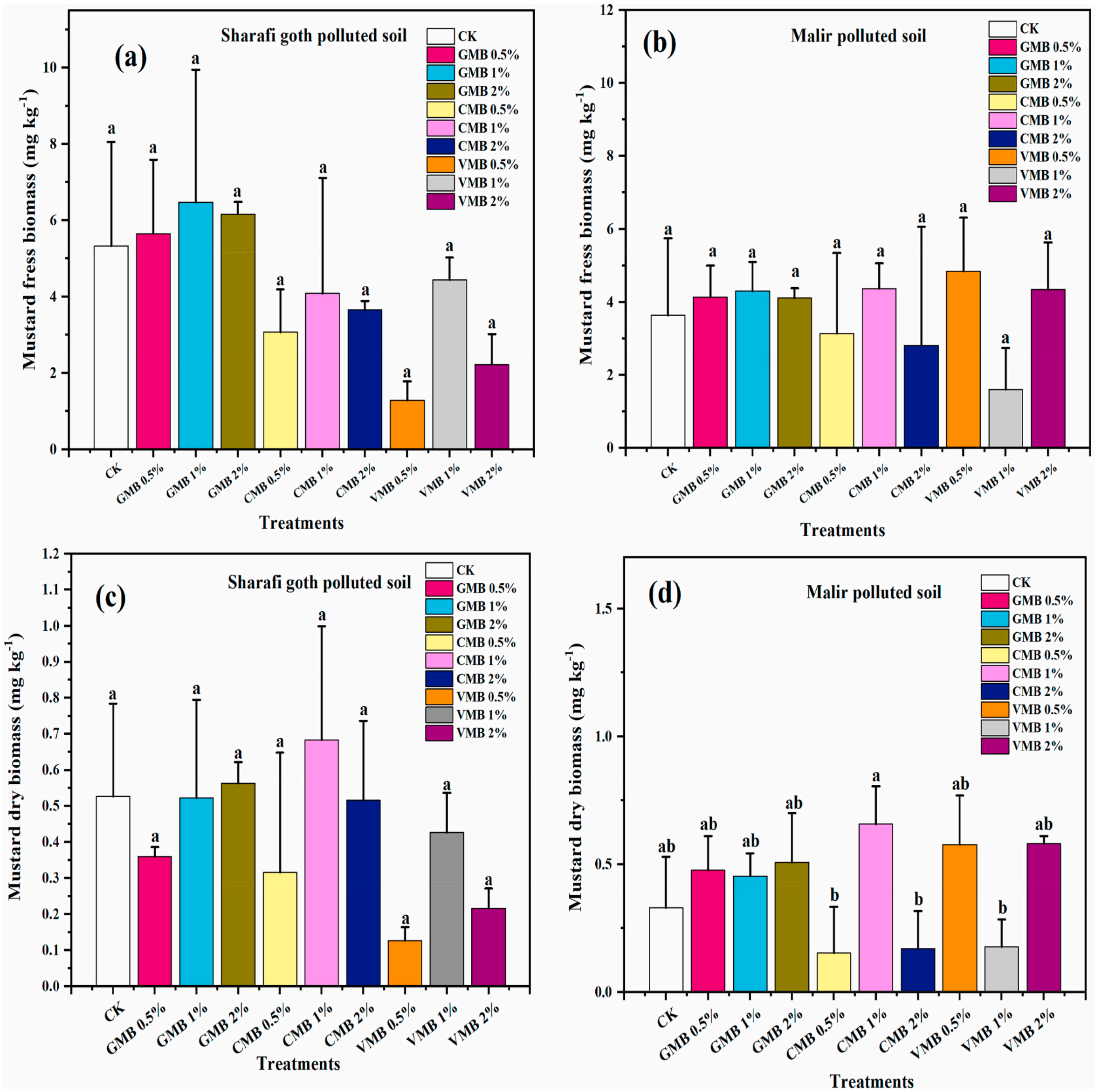


Fig. 3. Impact of modified biochars on: mustard fresh biomass in Sharafi goth polluted soil (a) and Malir polluted soil (b); mustard dry biomass in Sharafi goth polluted soil (c) and Malir polluted soil (d).

was higher after applying GMB in 0.5%, 1%, and 2% doses compared to other modified biochars. In addition, the application of GMB 1% in Sharafi goth polluted soil significantly increased the mustard fresh biomass, i.e. to 17.8%, whereas the lowest fresh biomass of mustard plant was noted by 75.98% with application of VMB 0.5% than control treatment (Fig. 3a). The greatest amount of fresh biomass of mustard plant was obtained with the application of VMB 0.5% and it accounted for 17.6% compared to the control. The application of VMB 1% to Malir polluted soil non-significantly reduced the fresh biomass of mustard plant to 17.6% as compared with control, followed by other modified biochars (Fig. 3b). Mustard dry biomass in Sharafi goth polluted soil increased insignificantly by 22.02% after adding CMB 1%; however, VMB in a low dose evidently reduced mustard dry biomass to 75.4% compared to the control treatment (Fig. 3c). The maximum (50%) mustard dry biomass was observed after applying CMB 1%, while the minimum parameter value (54.7%) was recorded after introducing CMB 0.5% as compared to the treatment without any amendments (Fig. 3d). According to Khan et al. (2017), the application of vegetable waste- and chicken manure-modified biochars significantly increased the biomass yield of pak choi as compared to the control treatment. Ali et al. (2019)

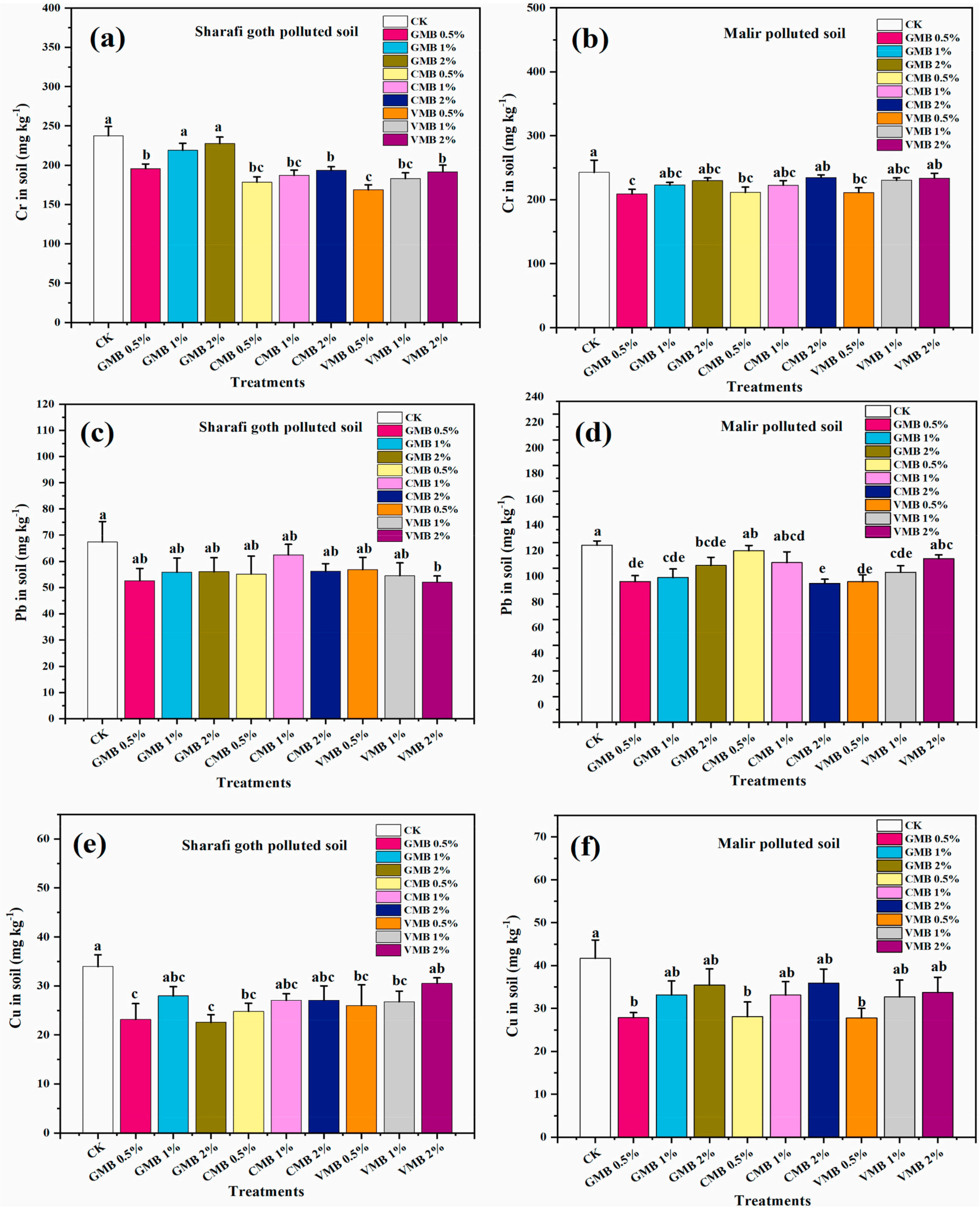


Fig. 4. Impact of modified biochars on: Cr in Sharafi goth polluted soil (a) and Malir polluted soil (b); Pb in Sharafi goth polluted soil (c) and Malir polluted soil (d); Cu in Sharafi goth polluted soil (e) and Malir polluted soil (f).

found that wheat plant growth was significantly increased following the application of wood BC in mining-polluted soil. However, Prapagdee et al. (2014) revealed that BC in a dose of 15% as a soil amendment caused opposite effects on plant growth.

3.6. *Impact of rock phosphate-modified biochars on Cr, Pb, and Cu in polluted soils*

The Cr, Pb, Cu, Zn, Ni, and Cd contents in Sharafi goth and Malir polluted soils were tested 50 days after mustard harvest. Cr in Sharafi Goth and Malir polluted soils was evidently immobilized, i.e. by 28.92% following the application of VMB 0.5% and by 13.92% after the application of GMB 0.5% as compared with control (Fig. 4a and b). The

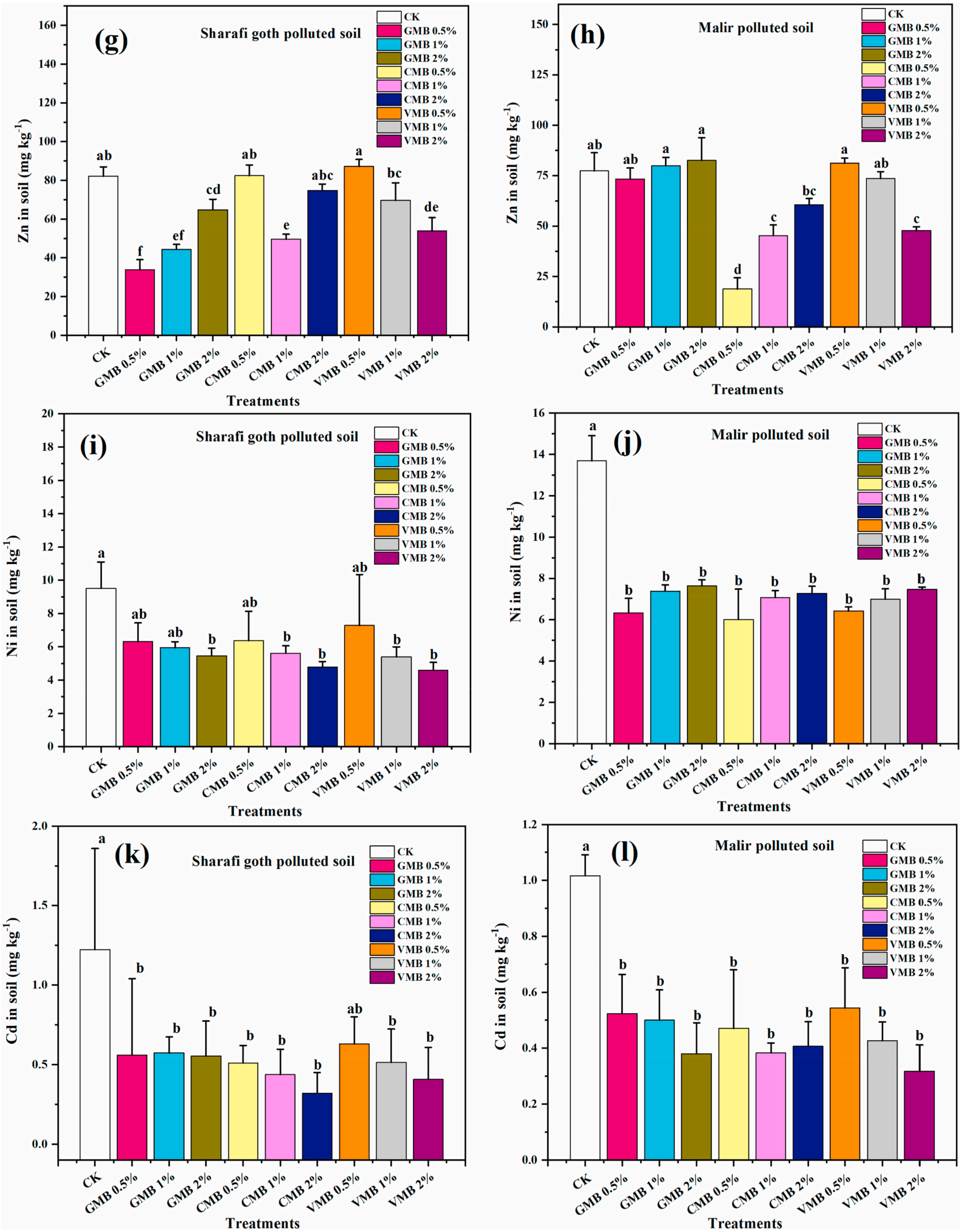


Fig. 5. Impact of modified biochars on: Zn in Sharafi goth polluted soil (g) and Malir polluted soil (h); Ni in Sharafi goth polluted soil (i) and Malir polluted soil (j); Cd in Sharafi goth polluted soil (k) and Malir polluted soil (l).

maximum immobilization of Pb in Sharafi goth polluted soil reached 22.65% with VMB 2%; similarly, the immobilization of Pb in Malir polluted soil was 21.63% with CMB 2% as compared with control (Fig. 4c and d). The Cu content in Sharafi goth polluted soil was significantly reduced to 33.55% with the application of GMB 2%. What is more, the Cu content in Malir polluted soil was substantially reduced to 33.3% after applying a low (0.5%) VMB dose compared to control (Fig. 4e and f). Ali et al. (2019) discovered that Pb and Cu in mining soil were clearly immobilized after adding wood BC, which was due to the increase in soil pH. Arabi et al. (2021) observed the immobilization of Cr in acidic soil following the application of wood BC. Lu et al. (2017) reported that BCs from bamboo and rice straw had the potential to bind metals with organic matter in treated samples. Luo et al. (2022) reported that P-composite BC exhibited higher Pb and Cd fixation potential

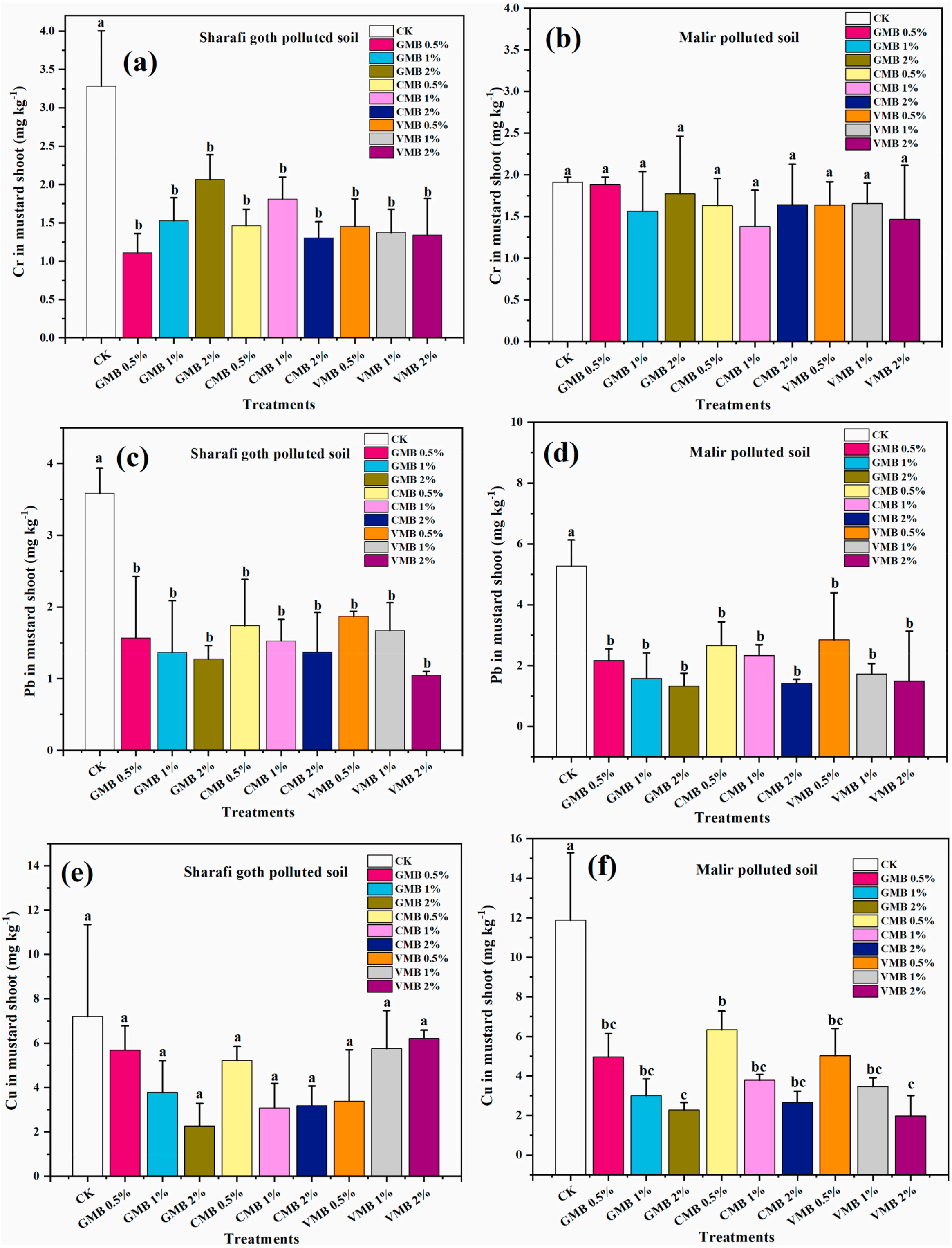


Fig. 6. Impact of modified biochars on: Cr in mustard shoots of Sharafi goth polluted soil (a) and Malir polluted soil (b); Pb in mustard shoots of Sharafi goth polluted soil (c) and Malir polluted soil (d); Cu in mustard shoots of Sharafi goth polluted soil (e) and Malir polluted soil.

(31.3–92.3%) than pristine BC (9.5–47.2%), which was mainly caused by the formation of stable precipitates such as $Pb_5(PO_4)_3Cl$ and $Cd_3(PO_4)_2$, particularly for the $Ca_5(PO_4)_3(OH)$ variant.

3.7. Impact of rock phosphate-modified biochars on Zn, Ni, and Cd in polluted soils

Compared to the control treatment, Zn in Sharafi goth polluted soil was significantly mobilized to 0.38% after the addition of CMB 0.5% and to 5.9% after applying VMB 0.5%, whereas the addition of GMB 0.5% caused immobilization of Zn by 58.73%. Also, Zn in Malir polluted soil was evidently mobilized to 3.15% with GMB 1%, 6.34% with GMB 2%, and 4.78% with VMB 0.5%; however, the maximum stabilization of Zn (75.73%) was observed after adding CMB 0.5%, as compared with control (Fig. 5g and h). The Ni content was significantly reduced, i.e. by 0.05%, after the application of VMB 2% to Sharafi goth polluted soil, and by 56.09% after the application of CMB 0.5% to Malir polluted soil, as compared with control (Fig. 5i and j). The maximum immobilization of Cd in Sharafi goth and Malir polluted soils reached 73.8% after the addition of CMB 2% and 68.7% after the addition of VMB 2% compared to control (Fig. 5k and l). It was observed that rock phosphate-modified biochars were more effective in immobilizing Cr, Pb, Cu, and Ni than Zn in Sharafi goth and Malir polluted soils, which may be due to the increase of OM in polluted soils. Liang et al. (2014) showed that the major mechanism underlying phosphate-induced PTE retention in soil was mainly due to metal-phosphate precipitation, while both sorption and precipitation were responsible for metal stabilization in BC addition. Puga et al. (2015) demonstrated that BC can retain huge proportions of PTEs in soil due to, among other things, its characteristics and large surface area. Ali et al. (2019) found that Zn and Cd in mining-polluted soil were markedly stabilized after the addition of wood BC, which may be caused by the increase in soil pH. However, Lu et al. (2017) reported that BC produced from rice straw and introduced at 5% evidently increased the organically bound Zn fraction in polluted soil. Arabi et al. (2021) stated that wood BC had the potential to immobilize Ni in acidic soils. Ge et al. (2022) found that the dominant fixation mechanism in their synergistic application was that H_3PO_4-modified hydrochar (BPH) could fix Pb, Cd, and Cu by precipitation, complexation, and π−π electron-donor-acceptor interaction.

3.8. Impact of rock phosphate-modified-biochars on Cr, Pb, and Cu uptake by mustard shoots

Cr uptake by shoots was highly significantly reduced (by 66.15%) when GMB 0.5% was applied in Sharafi goth polluted soil, while a non-significant (27.74%) reduction in Cr uptake by mustard was observed following the addition of CMB 1% to Malir polluted soil (Fig. 6a and b). The maximum Pb uptake by mustard shoots was significantly reduced (by 60.7%) after applying VMB 2% in Sharafi goth polluted soil as compared to control. Additionally, the greatest reduction of Pb in mustard shoots was observed following the application of GMB 2% in Malir polluted soil, which was 74.76% compared to the control treatment (Fig. 6c and d). The application of GMB 2% as an amendment in Sharafi goth polluted soil resulted in the maximum decrease in Cu uptake by mustard shoots, accounting for 68.7% compared to control. The highest reduction (83.41%) in Cu uptake by mustard shoots was determined after applying VMB 2% in Malir polluted soil as compared to the treatment without additives (Fig. 6e and f). The study by Ali et al. (2019) revealed that Pb and Cu uptake by wheat shoots was clearly reduced after application of wood BC, which was due to increase in soil pH. Letsoalo (2020) found that BC from acacia and poultry litter considerably reduced Cr uptake by spinach.

3.9. Impact of rock phosphate-modified biochars on Zn, Ni, and Cd uptake by mustard shoots

The maximum increase in the Zn content in mustard shoots (14.84%) was observed with the application of GMB1%, 29.32% with CMB 0.5%, and 29.8% with VMB 0.5%. On the other hand, the greatest reduction in Zn in mustard shoots (28.21%) was noted after the addition of CMB 2% in Sharafi goth polluted soil, as compared with control. It was observed that GMB 1%, CMB 0.5%, and VMB 0.5% had the potential to increase Zn uptake by a hyperaccumulator plant, and the main reason for this mechanism was reduced soil pH. Soils in Pakistan are 70% deficient in Zn, especially land used for the cultivation of rice, vegetables, and cotton. These rock phosphate-modified biochars, introduced at low rates, can be successfully used to enhance Zn mobility in industrially polluted soil and increase Zn uptake by plants. However, it was found that the high-dose application of CMB 2% reduced the Zn content in polluted soil due to an almost 1-fold increase in soil pH (Fig. 7 g). The maximum detected increase in Zn uptake by mustard shoots was: 1.8% with GMB 1%, 12.5% with GMB 2%, and 3.11% with CMB 0.5%; however, the application of VMB 2% reduced the Zn concentration in mustard shoots by 35% as compared with control. The above results indicated that GMB 1%, GMB 2%, and CMB substantially enhanced Zn uptake by plants as a result of lowering soil pH. Furthermore, VMB 2% in high dose reduced Zn uptake by the plant in Malir wastewater-treated soil, as soil pH increased up to 1.11 folds (Fig. 7h). Namgay et al. (2010) reported that the application of activated wood BC increased the concentration of Zn in maize plants.

Ni uptake by mustard shoots was significantly reduced to 86.36% following the application of GMB 2% in Sharafi goth polluted soil, and 76.44% reduction of Ni in mustard shoots was observed with the application of CMB 2% in Malir polluted soil, as compared to control (Fig. 7i and j). Compared to control, the maximum reduction of Cd concentration in mustard shoots was 89.41% after adding GMB 2% in Sharafi goth polluted soil; similarly, the maximum reduction of Cd in mustard shoots was 99.13% following the application of VMB 2% in Malir polluted soil (Fig. 7k and l). In this context, we hypothesized that MBs can stabilize PTEs in polluted soils, improve plant growth, and reduce PTE uptake by mustard. After introducing MBs into polluted soil, we compared the above results with our hypothesis and confirmed that PTEs were evidently immobilized Cr, Pb, Cu, Ni and Cd except Zn in soil-plant system, due to changes in soil chemical properties, including pH. Ali et al. (2019) applied wood BC in mining-polluted soil and observed that the accumulation of Zn and Cd in wheat shoots was significantly reduced with increasing pH. Letsoalo (2020) showed that BC from acacia and poultry litter significantly decreased Ni accumulation in spinach.

3.10. Redundancy analysis of the studied parameters

According to the obtained data, the relationships between EC, pH, OM, and SOC are indicated by red arrows and between fresh and dry biomass of mustard, Zn, Cd, Ni, Cr, Pb, and Cu in soil and maize shoots are indicated by blue arrows (Fig. 8a). RDA revealed that the studied parameters can explain (74.25%) of the total variance in Sharafi goth polluted soil. Soil pH was significantly negatively correlated with Zn in soil and mustard shoots. Similarly, soil EC, OM, SOC, and pH were significantly negatively correlated with Cu, Ni, Cd, Cr, and Pb in mustard plants and Shrafir goth polluted soil. In addition, EC showed a negative correlation with mustard fresh and dry biomasses. The data obtained for Malir polluted soil revealed that the studied parameters can explain (52.65%) of the total variance. The data showed that OM was significantly positively correlated with EC, pH, and Zn uptake in mustard shoots; however, a negative correlation of OM was observed with lead, cadmium, zinc, nickel, copper, and chromium in Malir polluted soil. Moreover, soil EC and pH were significantly negatively correlated with lead, cadmium, zinc, nickel, copper, and chromium in

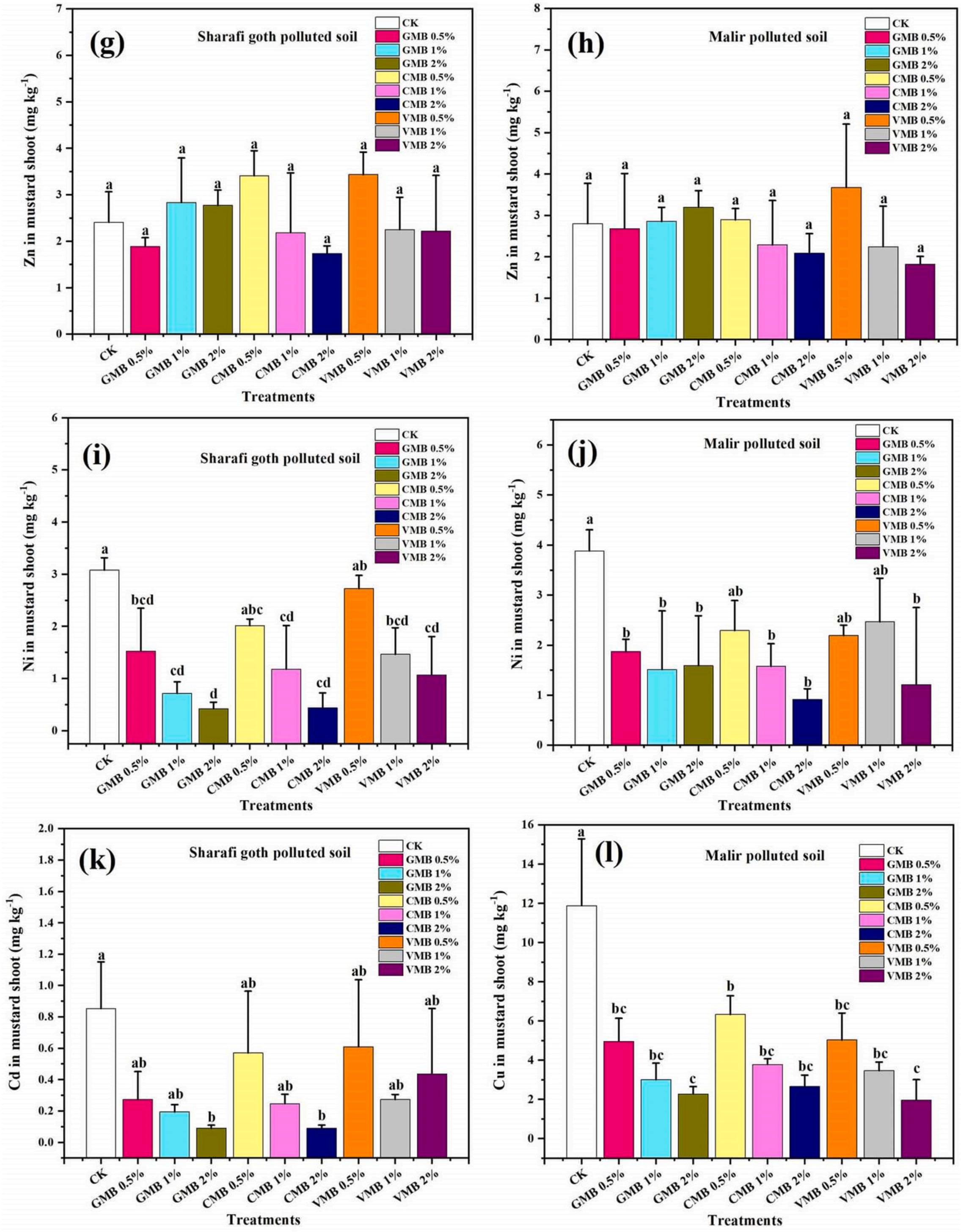


Fig. 7. Impact of modified biochars on: Zn in mustard shoots of Sharafi goth polluted soil (g) and Malir polluted soil (h); Ni in mustard shoots of Sharafi goth polluted soil (i) and Malir polluted soil (j).

Malir polluted soil and mustard shoots (Fig. 8b). A.H. Lahori et al. (2020) performed a redundancy analysis between PTEs and soil chemical properties using minerals and biochar. The obtained results indicated that the mobility and immobility of PTEs depend on soil chemical properties, soil type, and nature of additives.

4. Conclusions

The main objective of the present study was to assess the effectiveness of three different rock phosphate-modified BCs introduced in 0.5, 1, and 2% doses on PTE fixation in Sharafi goth and Malir polluted soils. The results indicated that modified BCs GMB 0.5%, GMB 1%, and GMB 2% increased the fresh biomass of mustard, but VMB 0.5% reduced the fresh biomass of mustard grown in Sharfi goth polluted soil. In addition, GMB 0.5%, GMB 1%, GMB 2%, VMB 0.5%, and VMB 2% potentially enhanced the fresh biomass of mustard, while VMB 1% reduced the fresh biomass of mustard in Malir polluted soil compared to control. Application of MBs potentially immobilized Cr, Pb, Cu, Ni, and

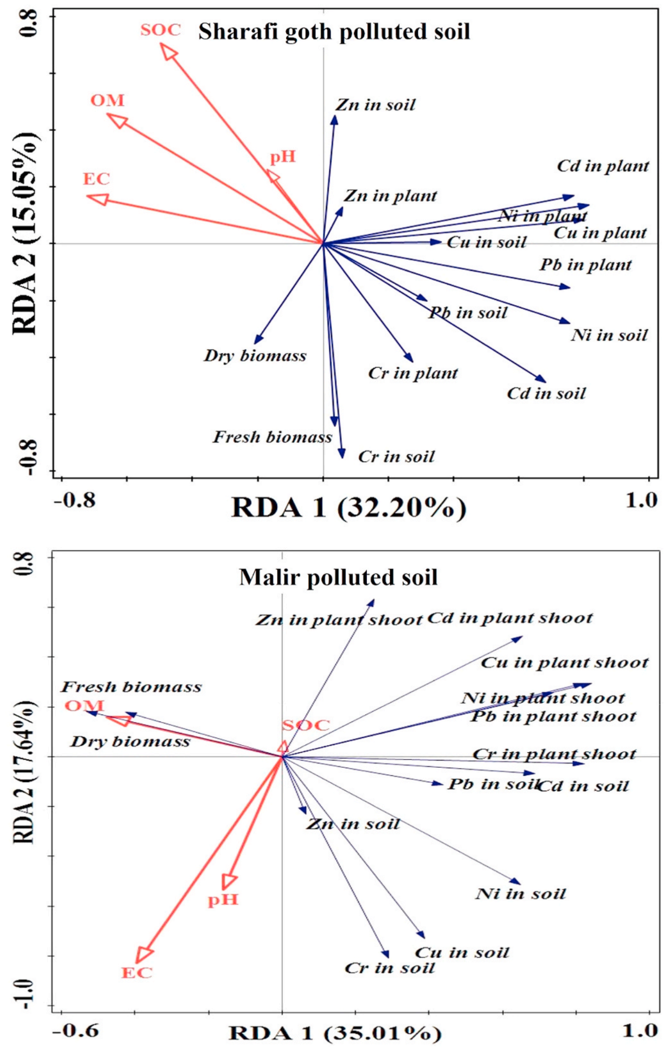


Fig. 8. Redundancy analysis of the studied parameters in polluted soils.

Cd in Sharafi goth and Malir polluted soils. However, CMB 0.5% and VMB 0.5% mobilized Zn in Sharafi goth polluted soil and GMB 1%, GMB 2%, and VMB 0.5% as amendments mobilized Zn in Malir wastewater-polluted soil. The uptake of Cr, Pb, Cu, Ni, and Cd by mustard shoots was significantly reduced; however, GMB 1%, CMB 0.5%, and VMB 0.5% treatments increased Zn uptake in Sharafi goth polluted soil and GMB 1%, GMB 2%, CMB 0.5%, and VMB 0.5% treatments caused the same in Malir polluted soil. This may be due to changes in EC, pH, OM, and SOC following the application of BCs. Soils in Pakistan are 70% deficient in Zn, especially land used for the cultivation of rice, vegetables, and cotton. It was further concluded that 0.5–1% BCs doses can be successfully used in Zn deficient areas, but 2% dose can stabilize Zn toxicity in polluted soils. Overall, the present study recommends long-term field experiments to verify the residual impact of MBs at different doses and particle sizes on the dominant mechanism of PTE fixation in polluted soils under various field crops. Future studies need to be carried out with BCs produced at different pyrolysis temperatures, in various doses, combined with other materials such as nanomaterials, minerals, etc. to evaluate their effect on soil enzymatic activity, macro-/micronutrient contents, molecular level, and stability of organic/inorganic contaminants from polluted areas.

Author contributions

Tanveer Hussain and Altaf Hussain Lahori: Conceptualization, Methodology and Writing – original draft; Monika Mierzwa- Hersztek: Investigation, Writing – review & editing; Samreen Riaz Ahmed and Viola Vambol: Investigation, Writing – review & editing; Muhammad Faizan Shahid: Writing – review & editing and Software; Altaf Hussain Lahori: Software and Validation; Asif Ali Khan: Writing – review & editing; Lubna Rafique: Formal analysis; Sajid wasia and Zhang Zengqiang: Formal analysis.

Conceptualization

Tanveer Hussain and Altaf Hussain Lahori.; **Data curation;** Tanveer Hussain.; **Formal analysis;** Muhammad Faizan Shahid.

Funding acquisition

Altaf Hussain Lahori.; **Investigation;** Samreen Riaz Ahmed and Viola Vambol.; **Methodology;** Tanveer Hussain, Altaf Hussain Lahori and Monika Mierzwa- Hersztek.; **Project administration;** Altaf Hussain Lahori.; **Resources;** Altaf Hussain Lahori.; **Software;** Altaf Hussain Lahori and Tanveer Hussain.; **Supervision;** Altaf Hussain Lahori.; **Validation;** Asif Ali Khan.; **Visualization;** Sajid Wasia and Zhang Zengqiang.; **Roles/Writing - original draft**; Altaf Hussain Lahori and Tanveer Hussain.; **Writing - review & editing.** Monika Mierzwa-Hersztek and Lubna Rafique.

Funding

In this present work, no any funding from any organization was received but was carried out from own expenses.

Declaration of competing interest

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.

Data availability

Data will be made available on request.

Acknowledgments

The authors are grateful to Dr. Khalida Batool, Department of English, University of Baltistan for proofreading the text.

References

Afzal, J., Hu, C., Imtiaz, M., Elyamine, A.M., Rana, M.S., Imran, M., Farag, M.A., 2018. Cadmium tolerance in rice cultivars associated with antioxidant enzymes activities and Fe/Zn concentrations. Int. J. Environ. Sci. Tech. 16, 4241. https://doi: 10.1007/s13762-018-2018-y.

Ahmad, M., Lee, S.S., Lee, S.E., Al-Wabel, M.I., Tsang, D.C.W., Ok, Y.S., 2017. Biochar-induced changes in soil properties affected immobilization/mobilization of metals/metalloids in contaminated soils. J. Soils Sediments 17 (3), 717–730. https://doi.org/10.1007/s11368-015-1339-4.

Ahmad, M., Lee, S.S., Lim, J.E., Lee, S.E., Cho, J.S., Moon, D.H., Ok, Y.S., 2014. Speciation and phytoavailability of lead and antimony in a small arms range soil amended with mussel shell, cow bone and biochar: EXAFS spectroscopy and chemical extractions. Chemosphere 95, 433–441. https://doi.org/10.1016/j.chemosphere.2013.09.077.

Ali, A., Guo, D., Jeyasundar, P.G.S.A., Li, Y., Xiao, R., Du, J., Zhang, Z., 2019. Application of wood biochar in polluted soils stabilized the toxic metals and enhanced wheat (Triticum aestivum L) growth and soil enzymatic activity. Ecotox. Eviron. Safe. 184, 109635 https://doi.org/10.1016/j.ecoenv.2019.109635.

Alshehri, S.M., Naushad, M., Ahamad, T., Alothman, Z.A., Aldalbahi, A., 2014. Synthesis, characterization of curcumin based ecofriendly antimicrobial bio-adsorbent for the removal of phenol from aqueous medium. Chem. Eng. J. (Lausanne) 254, 181–189. https://doi.org/10.1016/j.cej.2014.05.100.

Antoniadis, V., Levizou, E., Shaheen, S.M., Ok, Y.S., Sebastian, A., Baum, C., Prasad, M. N., Wenzel, W.W., Rinklebe, J., 2017. Trace elements in the soil-plant interface: phytoavailability, translocation, and phytoremediation–areview. Earth Sci. Rev. 171, 621–645. https://doi.org/10.1016/j.earscirev.2017.06.005.

Arabi, Z., Rinklebe, J., El-Naggar, A., Hou, D., Sarmah, A.K., Moreno-Jiménez, E., 2021. (Im) mobilization of arsenic, chromium, and nickel in soils via biochar: a meta-analysis. Environ. Pollut. 286, 117199 https://doi.org/10.1016/j.envpol.2021.117199.

Beiyuan, J., Li, J.S., Tsang, D.C., Wang, L., Poon, C.S., Li, X.D., Fendorf, S., 2017a. Fate of arsenic before and after chemical-enhanced washing of an arsenic-containing soil in Hong Kong. Sci. Total Environ. 599, 679–688. https://doi.org/10.1016/j.scitotenv.2017.04.208.

Beiyuan, J., Tsang, D.C., Ok, Y.S., Zhang, W., Yang, X., Baek, K., Li, X.D., 2016. Integrating EDDS-enhanced washing withlow-cost stabilization of metal-contaminatedunder -a waste recycling site. Chemosphere 426–432. https://doi.org/10.1016/j. chemosphere. 2016.06.030.

Beiyuan, J., Tsang, D.C., Valix, M., Baek, K., Ok, Y.S., Zhang, W., Bolan, N.S., Rinklebe, J., Li, X.-D., 2018. Combined application of EDDS and EDTA for removal of potentially toxic elements under multiple soil washing schemes. Chemosphere 205, 178–187. https://doi.org/10.1016/j.chemosphere.2018.04.081.

Beiyuan, J., Tsang, D.C., Valix, M., Zhang, W., Yang, X., Ok, Y.S., Li, X.D., 2017b. Selective dissolution followed by EDDS was hingofane-waste contaminated soil: extraction efficiency, fate of residual metals, and impact on soil environment. Chemosphere 489–496. https://doi.org/10.1016/j.chemosphere.2016.09.110.

Berihun, T., Tadele, M., Kebede, F., 2017. The application of biochar on soil acidity and other physico-chemical properties of soils in southern Ethiopia. J. Plant Nutr. Soil Sci. 180 (3), 381–388. https://doi.org/10.1002/jpln.201600343.

Cao, X., Harris, W., 2010. Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. Bioresour. Technol. 101, 5222–5228. https://doi.org/10.1016/j.biortech. 2010.02.052.

Caravaca, F., Alguacil, M.M., Azcon, R., Díazc, G., Roldána, A., 2004. Comparing the effectiveness of mycorrhizal inoculum and amendment with sugar beet, rock phosphate and Aspergillus Niger to enhance feld performance of the leguminous shrub Dorycnium pentaphyllum L. Appl. Soil Ecol. 25, 169–180 https://doi.org/10.1016/J.APSOIL. 2003.08.002.

Chao, X., Qian, X., Han-Hua, Z., Shuai, W., Qi-Hong, Z., Dao-You, H., Yang-Zhu, Z., 2018. Effect of biochar from peanut shell on speciation and availability of lead and zinc in an acidic paddy soil. Ecotoxicol. Environ. Saf. 164, 554–561. https://doi.org/10.1016/j.ecoenv. 2018.08.057.

Denneman, Robberse, 1990. Ministry of Housing, 1994; Source. WHO, Netherlands (1996).

Derakhshan-Nejad, Z., Jung, M.C., 2017. The effects of biochar and inorganic amendments on soil remediation in the presence of hyperaccumulator plant. Int. J. Energy Environ. Eng. 8 (4), 317–329. https://doi.org/10.1007/s40095-017-0250-8.

Downie, A., Crisky, A., Munroe, P., 2009. Physical properties of biochar. In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management: Science and Technology. Earthscan, London, U. K., pp. 13–32. https://doi.org/10.4324/9781849770552

Ge, Q., Tian, Q., Hou, R., Wang, S., 2022. Combing phosphorus-modified hydrochar and zeolite prepared from coal gangue for highly effective immobilization of heavy metals in coal-mining contaminated soil. Chemosphere 291, 132835. https://doi.org/10.1016/j. chemosphere.2021.132835.

Gholami, L., Rahimi, G., Khademi Jolgeh Nezhad, A., 2020. Effect of thiourea-modified biochar on adsorption and fractionation of cadmium and lead in contaminated acidic soil. Int. J. Phytoremediation 22 (5), 468–481. https://doi.org/10.1080/15226514.2019.1678108.

Glaser, B., Lehmann, J., Zech, W., 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal– a review. Biol. Fertil. Soils 35, 219–230. https://doi.org/10.1007/s00374-002-0466-4.

Gul, S., Whalen, J.K., Thomas, B.W., Sachdeva, V., Deng, H., 2015. Physico-chemical properties and microbial responses in biochar-amende,d soils: mechanisms and future directions. Agric. Ecosyst. Environ. 206, 46–59. https://doi.org/10.1016/j.agee.2015.03.015.

Hou, D., Al-Tabbaa, A., 2014. Sustainability: a new imperative in contaminated land remediation. Environ. Sci. Pol. 39, 25–34. https://doi.org/10.1016/j.envsci.2014.02.003.

Houben, D., Evrard, L., Sonnet, P., 2013. Beneficial effects of biochar application to contaminated soils on the bioavailability of Cd, Pb and Zn and the biomass production of rapeseed (Brassica napus L.). Biomass Bioenergy 57, 196–204. https://doi.org/10.1016/j.biombioe.2013.07.019.

Igalavithana, A.D., Lee, S.-E., Lee, Y.H., Tsang, D.C.W., Rinklebe, J., Kwon, E.E., Ok, Y.S., 2017. Heavy metal immobilization and microbial community abundance by vegetable waste and pine cone biochar of agricultural soils. Chemosphere 174, 593–603. https://doi.org/10.1016/j.chemosphere.2017.01.148.

Irshad, M.K., Noman, A., Alhaithloul, H.A.S., Adeel, M., Rui, Y.K., Shah, T., Zhu, S.S., Zhang, J.Y., 2020. Goethite modified Biochar ameliorates the growth of rice (Oryza sativa L.) plants by suppressing Cd and As-induced oxidative stress in Cd and as co-contaminated paddy soil. Sci. Total Environ. 717, 137086 https://doi.org/10.1016/j.scitotenv. 2020.137086.

Ishtiaq, M., Ahmad, I., 1987. The Potential of Hazara Phosphates for Phosphoric Acid Manufacture, vol. 14. Fertilizers research and development Institute, Faisalabad, Pakistan, pp. 257–263. https://doi.org/10.1007/BF01050670.

Karimi, A., Moezzi, A., Chorom, M., Enayatizamir, N., 2020. Application of biochar changed the status of nutrients and biological activity in a calcareous soil. J. Soil Sci. Plant Nutr. 20 (2), 450–459. https://doi.org/10.1007/s42729-019-00129-5.

Khalid, S., Shahid, M., Niazi, N.K., Murtaza, B., Bibi, I., Dumat, C., 2017. A comparison of technologies for remediation of heavy metal contaminated soils. J. Geochem. Explor. 182, 247–268. https://doi.org/10.1016/j.gexplo.2016.11.021.

Khan, K.Y., Ali, B., Cui, X., Feng, Y., Yang, X., Stoffella, P.J., 2017. Impact of different feedstocks derived biochar amendment with cadmium low uptake affinity cultivar of pak choi (Brassica rapa ssb. chinensis L.) on phytoavoidation of Cd to reduce potential dietary toxicity. Ecotox. Environ. Safe. 141, 129–138.

Kolton, M., Meller Harel, Y., Pasternak, Z., Graber, E.R., Elad, Y., Cytryn, E., 2011. Impact of biochar application to soil on the root-associated bacterial community structure of fully developed greenhouse pepper plants. Appl. Environ. Microbiol. 77 (14), 4924–4930. https://doi/10.1128/AEM.00148-11.

Komkiene, J., Baltrenaite, E., 2016. Biochar as adsorbent for removal of heavy metal ions [Cadmium (II), Copper (II), Lead (II), Zinc (II)] from aqueous phase. Int. J. Environ Sci. Tech. 13 (2), 471–482. https://doi.org/10.1007/s13762-015-0873-3.

Kuppusamy, S., Palanisami, T., Megharaj, M., Venkateswarlu, K., Naidu, R., 2016. Ex-situ remediation technologies for environmental pollutants: a critical perspective. Rev. Environ. Contam. Toxicol. 236, 117–192. https://doi.org/10.1007/978-3-319-20013-2_2.

Lahori, A.H., Mierzwa-Hersztek, M., Demiraj, E., Idir, R., Bui, T.T.X., Vu, D.D., Zhang, Z., 2020. Clays, limestone and biochar affect the bioavailability and geochemical fractions of cadmium and zinc from Zn-smelter polluted soils. Sustainability 12 (20), 8606. https://doi.org/10.3390/su12208606.

Lahori, A.H., Guo, Z., Zhang, Z., Ronghua, L.I., Jiang, S., 2017. Use of biochar as an amendment for remediation of heavy metal-contaminated soils: prospects and challenges. Pedosphere 27, 991–1014. https://doi.org/10.1016/S1002-0160(17)60490-9.

Lahori, A.H., Memon, K.S., Memon, M., Vambol, V., Yasoob, H., Aziz, A., Naheed, Z., 2019. Enhancing phosphorus solubility from rock phosphate integrated with farmyard manure in p-deficient soil. Labor. Protec. Probl. Ukraine. 35 (2), 8–14. https://doi.org/10.36804/nndipbop.35-2.2019.8-14.

Lahori, A.H., Mierzwa-Hersztek, M., Demiraj, E., Sajjad, R.U., Ali, I., Shehnaz, H., Aziz, A., Zuberi, M.H., Pirzada, A.M., Hassan, K., Zhang, Z.Q., 2020. Direct and residual impacts of zeolite on the remediation of harmful elements in multiple contaminated soils using cabbage in rotation with corn. Chemosphere 250, 126317. https://doi.org/10.1016/j. chemosphere. 2020.126317.

Letsoalo, M.L., 2020. The Effect of Biochar on Immobilization and Phytoavailability of Chromium, Nickel and Lead in Soils Amended with Slag (Doctoral Dissertation).

Li, J.S., Wang, L., Cui, J.L., Poon, C.S., Beiyuan, J., Tsang, D.C., Li, X.D., 2018. Effects of low-alkalinity binders on stabilization/solidification of geogenic As-containing soils: spectroscopic investigation and leaching tests. Sci. Total Environ. 631, 1486–1494. https://doi.org/10.1016/j.scitotenv.2018.02.247.

Liang, Y., Cao, X., Zhao, L., Arellano, E., 2014. Biochar-and phosphate-induced immobilization of heavy metals in contaminated soil and water: implication on simultaneous remediation of contaminated soil and groundwater. Environ. Sci. Pollut. Res. 21 (6), 4665–4674. https://doi.org/10.1007/s11356-013-2423-1.

Lindsay, W.L., Norvell, W.A., 1978. Development of a DTPA soil test for zinc, iron, manganese, and copper. Soil Sci. Soc. Am. J. 42, 421–428. https://doi.org/10.2136/SSSAJ1978. 03615995004200030009X.

Lu, K., Yang, X., Gielen, G., Bolan, N., Ok, Y.S., Niazi, N.K., Wang, H., 2017. Effect of bamboo and rice straw biochars on the mobility and redistribution of heavy metals (Cd, Cu, Pb and Zn) in contaminated soil. J. Environ. Manag. 186, 285–292. https://doi.org/10.1016/j. jenvman.2016.05.068.

Luo, Y., Li, Z., Xu, H., Xu, X., Qiu, H., Cao, X., Zhao, L., 2022. Development of phosphorus composite biochar for simultaneous enhanced carbon sink and heavy metal immobilization in soil. Sci. Total Environ. 831, 154845 https://doi.org/10.1016/j.scitotenv.2022.154845.

Mebius, L.J., 1960. A rapid method for the sdetermination of organic carbon in soil. Analytica Chimica Acta 22, 120–124. https://doi.org/10.1016/S0003-2670(00)88254-9.

Namgay, T., Singh, B., Singh, B.P., 2010. Influence of biochar application to soil on the availability of As, Cd, Cu, Pb, and Zn to maize (Zea mays L.). Soil Res. 48 (7), 638–647. https://doi.org/10.1071/SR10049.

Novak, J.M., Cantrell, K.B., Watts, D.W., 2013. Compositional and thermal evaluation of lignocellulosic and poultry litter chars via high and low temperature pyrolysis. Bioener. Res. 6 (1), 114–130. https://doi.org/10.1007/s12155-012-9228-9.

Palansooriya, K.N., Shaheen, S.M., Chen, S.S., Tsang, D.C.W., Hashimoto, Y., Hou, D., Bolan, N.S., Rinklebe, J., Ok, Y.S., 2020. Soil amendments for immobilization of potentially toxic elements in contaminated soils: a critical review. Environ. Int. 134, 105046 https://doi.org/10.1016/j.envint.2019.105046.

Park, J.H., Lamb, D., Paneerselvam, P., Choppala, G., Bolan, N., Chung, J.W., 2011. Role of organic amendments on enhanced bioremediation of heavy metal (loid) contaminated soils. J. Hazard Mater. 185 (2–3), 549–574. https://doi.org/10.1016/j.jhazmat.2010.09.082.

Prapagdee, S., Piyatiratitivorakul, S., Petsom, A., Tawinteung, N., 2014. Application of biochar for enhancing cadmium and zinc phytostabilization in Vigna radiata L. cultivation. Water, Air. & Soil Pollution 225 (12), 1–13. https://doi.org/10.1007/s11270-014-2233-1.

Puga, A.P., Abreu, C.A., Melo, L.C.A., Paz-Ferreiro, J., Beesley, L., 2015. Cadmium, lead, and zinc mobility and plant uptake in a mine soil amended with sugarcane straw biochar. Environ. Sci. Pollut. Res. 22 (22), 17606–17614. https://doi.org/10.1007/s11356-015-4977-6.

Puga, A.P., Abreu, C.A., Melo, L.C.A., Beesley, L., 2015. Biochar application to a contaminated soil reduces the availability and plant uptake of zinc, lead and cadmium. J. Environ. Manag. 159, 86–93. https://doi.org/10.1016/j.jenvman.2015.05.036.

Qiao, D.H., Wang, G.S., Li, X.S., Wang, S., Zhao, Y.Y., 2020. Pollution, sources and environmental risk assessment of heavy metals in the surface AMD water, sediments and surface soils around unexploited Rona Cu deposit, Tibet, China. Chemosphere 248, 125988. https://doi.org/10.1016/j.chemosphere.2020.125988.

Rahman, M., Muhammad, D., Mussarat, M., Sharif, M., Irfan, M., Ahmad, J., Ishaq, F., 2018. Effect of acidulated levels and application techniques of rock phosphate on phosphorus use efficiency and yield of wheat in calcareous soil of Peshawar-Pakistan. Pure appl. biol. 7 (3), 1094–1103. https://doi.org/10.19045/bspab.2018.700128.

Rajendran, S., Priya, T.A.K., Khoo, K.S., Hoang, T.K., Ng, H.S., Munawaroh, H.S.H., Show, P.L., 2022. A critical review on various remediation approaches for heavy metal contaminants removal from contaminated soils. Chemosphere 287, 132369. https://doi.org/10.1016/j.chemosphere.2021.132369.

Ren, J., Zhao, Z.X., Ali, A., Guan, W.D., Xiao, R., Wang, J.J., Ma, S.R., Guo, D., Zhou, B. Y., Zhang, Z.Q., Li, R.H., 2020. Characterization of phosphorus engineered biochar and its impact on immobilization of Cd and Pb from smelting contaminated soils. J. Soils Sediments 20, 3041–3052. https://doi.org/10.1007/s11368-019-02403-6.

Rinklebe, J., Shaheen, S.M., 2015. Miscellaneous additives can enhance plant uptake and affect geochemical fractions of copper in a heavily polluted riparian grassland soil. Ecotox. Environ. Safe. 119, 58–65. https://doi.org/10.1016/j.ecoenv.2015.04.046.

Taskin, E., de Castro Bueno, C., Allegretta, I., Terzano, R., Rosa, A.H., Loffredo, E., 2019. Multianalytical characterization of biochar and hydrochar produced from waste biomasses for environmental and agricultureural applications. Chemosphere 233, 422–430. https://doi.org/10.1016/j.chemosphere.2019.05.204.

The United States Environmental Protection Agency (EPA), 1996. Method 3050B: acid digestion of sediments, sludges, and soils. Revision 2.

Wang, L., Chen, S.S., Sun, Y., Tsang, D.C., Yip, A.C., Ding, S., Hou, D., Baek, K., Ok, Y.S., 2018. Efficacy and limitations of low-cost adsorbents for in-situ stabilisation of contaminated marine sediment. J. Clean. Prod. 212, 420–427. https://doi.org/10.1016/j. jclepro.2018.12.056.

Wang, L., Kwok, J.S., Tsang, D.C., Poon, C.-S., 2015. Mixture design and treatment methods for recycling contaminated sediment. J. Hazard Mater. 283, 623–632. https://doi.org/10.1016/j.jhazmat.2014.09.056.

Wang, Q., Shaheen, S.M., Jiang, Y., Li, R., Slaný, M., Abdelrahman, H., Zhang, Z., 2021. Fe/Mn-and P-modified drinking water treatment residuals reduced Cu and Pb phytoavailability and uptake in a mining soil. J. Hazard Mater. 403, 123628 https://doi.org/10.1016/j.jhazmat.2020.123628.

Who, 2016. News Release, Geneva. http://www.who.int/news-room/detail/1503-2016-an-estimated-12-6-million-deaths-each-year-are-attributable-to-unhealthy environments.

World Health Organization, 1996. The World health report : 1996 : fighting disease, fostering development / report of the Director-General. World Health Organization. World Health Organization 1–137. https://apps.who.int/iris/handle/10665/36848.

Xu, W.Q., Pignatello, J.J., Mitch, W.A., 2013. The role of black carbon electrical conductivity in mediating hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) transformation on carbon surfaces by sulfides. Environ. Sci. Technol. 47, 7129–7136. https://doi.org/10.1021/es4012367.

Zhang, H., Shao, J., Zhang, S., Zhang, X., Chen, H., 2020. Effect of phosphorus-modified biochars on immobilization of Cu (II), Cd (II), and as (V) in paddy soil. J. Hazard Mater. 390, 121349 https://doi.org/10.1016/j.jhazmat.2019.121349.

Zhang, M., Riaz, M., Zhang, L., El-Desouki, Z., Jiang, C., 2019. Biochar induces changes to basic soil properties and bacterial communities of different soils to varying degrees at 25 mm rainfall: more effective on acidic soils. Front. Microbiol. 10, 1321. https://doi.org/10.3389/fmicb.2019.01321.

Zhu, G., Xiao, H., Guo, Q., Song, B., Zheng, G., Zhang, Z., Zhao, J., Okoli, C.P., 2018. Heavy metal contents and enrichment characteristics of dominant plants in wasteland of the downstream of a lead-zinc mining area in Guangxi, Southwest China. Ecotox. Environ. Safe. 151, 266–271. https://doi.org/10.1016/j.ecoenv.2018.01.011.