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The Application of MgO-Modified Biochars for the Immobilization of Ni, Cu, Pb, and Cr in Stone Crushing and Mining-Polluted Soil

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Abstract: The objective of the present study was to investigate the impact of MgO 0.5 g/kg loaded in different organic waste materials on the properties of the modified biochars obtained. The waste materials included tea waste, wood waste, water chestnut peel, and pomegranate peel, which were used to create tea waste MgO-modified biochar (TWMgO-MBC), wood waste MgO-modified biochar (WSMgO-MBC), water chestnut peel MgO-modified biochar (WCMgO-MBC), and pomegranate peel MgO-modified biochar (PPMgO-MBC). All the MgO-modified biochars were prepared at 600 °C for 2 h and applied at 0.5 and 1% doses for the immobilization of Ni, Cu, Pb, and Cr in stone crushing and mining-polluted soil and the reduction in their uptake by pearl millet (*Pennisetum glaucum*) plant. The greatest fresh and dry biomasses were observed at 45.04% and 31.29%, respectively, with the application of TWMgO-MBC 1% in stone-crushing-polluted soil. The highest degree of immobilization of Ni (76.67%) was observed for the WSMgO-MBC 1% treatment, Cu (73.45%) for WCMgO-MBC 1%, Pb (76.78%) for WSMgO-MBC 1%, and Cr (70.55%) for WCMgO-MBC 1%, in comparison with the control. The maximum uptake of Ni, Cu, Pb, and Cr in the shoot of pearl millet was reduced by 78.43% with WSMgO-MBC 1%, 75.06% with WSMgO-MBC 1%, 90.81% with WCMgO-MBC 1%, and 85.71% with WSMgO-MBC 1% as compared with the control. The greatest reduction in Ni, Cu, Pb, and Cr in the root of pearl millet was observed at 77.81% with WSMgO-MBC 1%, 68.09% with WCMgO-MBC 1%, 84.03% with WCMgO-MBC 1%, and 88.73% with WCMgO-MBC 1%, in comparison with the control. The present study demonstrated that the TWMgO-MBC 1% treatment was highly effective for improving plant growth, while the WSMgO-MBC 1%, and WCMgO-MBC 1% treatments were found to be highly effective for immobilizing heavy metals in polluted soils, thus facilitating safe crop cultivation. Future studies should concentrate on the long-term application of MgO-modified biochars for the remediation of multimetal-polluted soils.

Keywords: modified biochars; immobilization; soil restoration; soil health; peal millet biomass

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1. Introduction

The heavy metal pollution of soil has become a severe global problem, with these pollutants not being naturally biodegradable. Such contamination can have a significant impact on the environment and human health [1–3]. The expansion of global economic activity, the growth of mining operations, the development of modern industrial and agricultural practices, and the discharge of untreated sewage sludge and zinc smelting in developing countries have contributed to the accumulation of metals in soil, including nickel, copper, lead, and chromium [4]. These metals can affect soil health, microbial growth, seedling germination, plant growth/fruiting, and crop quality. The accumulation of metals from soil to plant body can deteriorate aquatic life, water quality, and animal and human health through the food chain [5,6]. Exposure to these metals in excess can result in significant health issues, including kidney damage, anemia, and damage to the nervous system and development. This occurs through a process known as biomagnification, whereby the metals accumulate in the human body over time [7]. High soil concentrations of these harmful metals can stress vegetable plants and soil microbial communities, lowering agricultural productivity and interfering with ecosystem processes [8]. Furthermore, plant development, oxidative stress markers, and photosynthetic pigments are among the physiological and biochemical aspects of plants that are impacted by toxic metal poisoning, rendering them unsafe for human consumption and food security [9,10].

Immobilization is an effective and robust approach with the potential to remediate polluted soils through the conversion of soluble metal forms to insoluble forms, as compared with traditional physical and chemical methods [11,12]. It is also more cost-effective, environmentally friendly, versatile, and fast to implement [13]. It has the potential to be applied to a significant extent for the restoration of polluted soils in China [14–16]. The use of productive and payable additives is essential for the successful implementation of immobilization, as they can modify soil chemical properties to stabilize metals and reduce their uptake by plants, thus ensuring safe crop production [17]. For this reason, it is crucial to develop a high-performing, low-cost method for remediating heavy-metal-polluted soil in order to safeguard public health [3]. Biochar is a solid and carbon-rich material with promising properties that has been widely used for the stabilization of metals in polluted soil and the improvement of soil health [18]. Biochar can be produced from the conversion of organic waste material through pyrolysis in the absence of oxygen [19]. Biochar offers a multitude of benefits, including low cost, the stabilization of metals in soil, the capture of carbon, and the enhancement of moisture content, organic matter, nutrients, and plant growth, as well as soil microbial activity. This is due to its high surface area, macro/microporosity, and functional groups [20,21]. The literature indicates that biochar is highly effective for the immobilization of metals in soil [22–26]. Nevertheless, the application of biochar alone is not as effective as that of modified biochars in stabilizing metals in multi-metal polluted soil. The immobilization of biochar in soil for the stabilization of heavy metals can be based on electrostatic interaction, ion exchange, pore filling, precipitation, and complexation [27]. However, the efficiency of the immobilization mechanism in soil is dependent on the type of feedstock, particle dose, aging factor, soil temperature, cation exchange, soil moisture, and soil type [28]. On the other hand, the high application dose of biochar may compact soil particles and exert a detrimental impact on soil health, reduce microbial dynamics, absorb nutrients, especially fresh biochar, and reduce plant growth through increasing soil pH. Ghassemi-Golezani and Rahimzadeh [29] reported that biochar is an environmentally friendly and economically viable soil material. The addition of modifiers, such as physical and chemical modifications, impregnation with mineral sorbents, and magnetic modifications in the feedstock, can result in the production of modified biochar that can improve its functionality for the efficient remediation of polluted soils. The application of modified biochar in soil represents a novel approach that has the potential to enhance soil health, quality, plant growth, and the immobilization of multimetal in polluted soils, thereby facilitating sustainable agriculture [30].

Previous studies have investigated the removal of pollutants in water and wastewater using modified biochars [31–33], with a focus on the application of these materials in water treatment. However, only a few studies have been conducted with the specific aim of soil remediation [34–36]. Therefore, it is crucial to identify an effective modified biochar for the remediation of multimetal polluted soil. In their former study, García et al. [37] proposed that low-grade MgO has the potential to be an effective, long-term, and economically feasible additive for the stabilization of heavy metals in heavily polluted soil. This is due to its ability to act as a buffering agent within the pH range of 9–11, which reduces the solubility of heavy metals and prevents the redissolution of heavy metals in polluted sites. Lu et al. [38] evaluated the impact of magnetic and conventional poultry litter and Eucalyptus-made biochar at 300 and 500 °C on the stabilization of Cd, Cu, Zn, and Pb in multimetal polluted soil. Shen et al. [39] investigated the efficacy of MgO-coated corncob biochar (MCB) on the stabilization of Pb in soil and water. Bao et al. [40] reviewed that modification can enhance the activity of specific functional groups of biochar. Furthermore, biochar has the potential to adjust soil pH and nutrient retention and enhance moisture levels and soil enzymatic activity. Li et al. [41] examined the potential of MgO flake-modified biochar for the removal of Cd(II), Cu(II), Zn(II), and Cr(VI) in soil and aqueous water. Su et al. [42] assessed the effectiveness of Mn-modified bamboo biochar in immobilizing Pb, As, Cd, and Cu in polluted soil and improving soil health.

A paucity of studies has been conducted on the application of MgO-modified biochar in the remediation of stone crushing and mining-polluted soils. In the present study, MgO was loaded at a concentration of 0.5 g/kg in tea waste, wood waste, water chestnut peel, and pomegranate peel to create tea waste MgO-modified biochar (TWMgO-MBC), wood waste MgO-modified biochar (WSMgO-MBC), water chestnut peel MgO-modified biochar (WCMgO-MBC), and pomegranate peel MgO-modified biochar (PPMgO-MBC). The obtained biochars were then evaluated for their efficacy in immobilizing Ni, Cu, Pb, and Cr in stone crushing and mining-polluted soil, as well as in reducing the uptake of these metals by pearl millet, a process that has not been well studied to date. The objective of the present study was to (1) examine the impact of tea waste MgO-modified biochar (TWMgO-MBC), wood waste MgO-modified biochar (WSMgO-MBC), water chestnut peel MgO-modified biochar (WCMgO-MBC), and pomegranate peel MgO-modified biochar (PPMgO-MBC) at 0.5 and 1% on the immobilization of Ni, Cu, Pb, and Cr in stone-crushing-polluted soil (Hub River Road) and mining-polluted soil (Industrial Mineral Grinding, Gaddani, Lasbela, Balochistan) and the reduction in these metals' uptake by pearl millet (*Pennisetum glaucum*) plant, as well as (2) assess the impact of the studied biochars on soil EC, pH, $CaCO_3$, CEC, OM, PD, BD, and DOC. The hypothesis was that the application of different MgO-modified biochars would exhibit disparate dissimilarities in the immobilization of different types of heavy metals, such as Ni, Cu, Pb, and Cr, in stone crushing and mining-polluted soils and diminish their uptake by the test crop, pearl millet, for sustainable agriculture. The purpose of this study is to ascertain the potential of utilizing plant components for the production of biofuels.

2. Materials and Methods

2.1. Area of Study

In the present study, soil samples were collected from two locations: Hub River Road (25°01′05″ N, 67°01′13″ E) (stone-crushing-polluted soil) and an industrial mineral grinding site in the vicinity of Gaddani, Lasbela, Balochistan (25°05′53″ N, 66°48′55″ E) (mining-polluted soil). The stone-crushing soil was found to be polluted due to the presence of waste dumping and stone-crushing units in close proximity to both roadsides. This has led to the accumulation of metals on the soil surface, which in turn has contaminated the soil. However, the mining soil was observed to be polluted due to the mining of minerals, tile cutting, and marble manufacturing industrial waste. Furthermore, it was noted that there is currently no awareness in Karachi, a megacity, of soil remediation techniques that employ environmentally friendly additives.

2.2. Soil Sampling

Composite surface soil samples (0–20 cm deep) were collected from various locations within both polluted soils to determine the soil physicochemical properties and pollution levels and to implement remediation strategies with MgO-modified biochars. The homogenized soil samples were air-dried for 4–5 days at room temperature under shadow conditions. All nonsoil material and debris were manually removed from the polluted soil samples. After drying, the soil samples were manually mixed and 2 mm sieved to prepare them for analysis of their physical and chemical properties, as well as their metal content. The physicochemical properties of both polluted soils are indicated in Table 1.

2.3. Material Collection and Preparation of MgO-Modified Biochars

In this study, MgO in the solid state was purchased from Urdu Bazar, Karachi. The tea waste was collected from a nearby tea or coffee shop. Furthermore, wood waste was collected from a local carpenter shop. Water chestnut peels were gathered from the nearby fruit and vegetable market, and pomegranate peels were collected from a juice shop in Karachi, Pakistan. In order to prepare modified biochars, 0.5 g/kg of MgO was blended in tea waste, wood waste, water chestnut peel, and pomegranate peel and pyrolyzed at 600 °C for 2 h in the absence of O_2 in a muffle furnace, resulting in the following products: tea waste MgO-modified biochar (TWMgO-MBC), wood waste MgO-modified biochar (WSMgO-MBC), water chestnut peel MgO-modified biochar (WCMgO-MBC), and pomegranate peel MgO-modified biochar (PPMgO-MBC) [43,44]. The yield of all the BCs was recorded after the pyrolysis process was complete in the muffle furnace. Table 1 presents the physicochemical properties of the MgO-modified biochars.

Table 1. Basic chemical characteristics of soils and MgO-modified biochars.

Parameters	SCPS	MPS	TWMgO-MBC	WSMgO-MBC	WCMgO-MBC	PPMgO-MBC	Soil Environmental Quality Standards *
pH	7.2 ± 0.2	7.4 ± 0.1	8.5 ± 0.8	8.8 ± 0.6	9.1 ± 1	8.9 ± 0.9	-
EC dS/cm	2.11 ± 1	2.90 ± 0.3	2.10 ± 0.6	1.90 ± 1	1.95 ± 0.2	1.40 ± 0.1	-
OM (%)	0.87 ± 0.9	0.76 ± 0.2	-	-	-	-	-
CEC	11.14 ± 0.7	8.49 ± 0.1	-	-	-	-	-
$CaCO_3$ (%)	9.21 ± 0.5	4.01 ± 0.3	-	-	-	-	-
Organic carbon (mg kg^{-1})	19.3 ± 0.4	15.8 ± 0.3	33.4 ± 0.1	21.1 ± 0.3	23.6 ± 0.2	19.8 ± 0.4	-
Dissolved organic carbon (mg kg^{-1})	17.9 ± 1	10.4 ± 0.2	31.2 ± 0.5	19.6 ± 0.4	16.1 ± 0.1	14.8 ± 0.7	-
Particle density (g/cm^3)	2.34 ± 0.4	2.51 ± 0.9	-	-	-	-	-
Buk density (g/cm^3)	1.39 ± 0.6	1.48 ± 0.2	-	-	-	-	-
Total (Ni mg/kg)	47.6 ± 0.8	63.9 ± 0.3	nd	0.008 ± 0.002	0.1 ± 0.004	nd	40
Total (Cu mg/kg)	51.1 ± 0.3	76.3 ± 0.1	0.002 ± 0.001	0.04 ± 0.006	0.09 ± 0.008	0.03 ± 0.002	35
Total (Pb mg/kg)	91.4 ± 0.1	88.5 ± 0.7	nd	0.006 ± 0.001	0.3 ± 0.002	nd	35
Total (Cr mg/kg)	129.8 ± 0.9	147.4 ± 0.2	nd	0.03 ± 0.009	0.07 ± 0.01	nd	90
Biochar yield g/100g	-	-	33.7 ± 0.3	34.5 ± 0.8	31.8 ± 0.7	32.7 ± 1	-

Legend: SCPS = stone-crushing-polluted soil, MPS = mining-polluted soil, TWMgO-MBC = tea waste MgO-modified biochar, WSMgO-MBC = wood waste MgO-modified biochar, WCMgO-MBC = water chestnut peel MgO-modified biochar, PPMgO-MBC = pomegranate peel MgO-modified biochar, nd = not detected. * State Environmental Protection Administration of China [45], environmental quality standards for soil natural background, the GB15618-1995 standards.

2.4. Experimental Set-Up

The present study examined the impact of MgO-modified biochars on the immobilization of Ni, Cu, Pb, and Cr in stone crushing and mining-polluted soil. Pearl millet was chosen as the crop to assess the phytoavailability of Ni, Cu, and Cr in the root and shoot biomasses by plants after the application of modified biochars in both polluted soils. All the prepared MgO-modified biochars were <1 mm sieved and applied at a rate of 0.5 and 1% to 1 kg of soil in both polluted soils [46]. After mixing the amendments in both polluted soils, the soil with 60% field capacity was maintained with distilled water and incubated at room temperature for 1 week, with the aim of observing a chemical reaction in the soil following the treatment. The studied MgO-modified biochars were carefully mixed with 9 treatments in 3 replicates in a complete randomized design (CRD). The application rate and treatment code are indicated in Table 2. Approximately 8 certified pure seeds of pearl millet were sown in each pot, and the soil moisture content was maintained at 80% throughout the seed germination period. Following germination, the soil field capacity was maintained at 65% moisture content with distilled water, with any lost water replenished on a daily basis throughout the experimental trial. One week after germination, the plants were thinned and allowed to grow to 5 healthy plants per pot. All the plants were harvested after 30 days of growth. During harvesting, the plants were uprooted from each pot, and the root and shoot biomasses were carefully separated. The plants were cleaned with distilled water, and the moisture was removed with tissue paper. The fresh biomass total (root and shoot) was then noted with a digital weighing balance machine. After that, the plant biomass was dried in an oven for 3 days. The dry biomass was subsequently noted after the drying process. The plant biomass was then ground in a small grinder mill, and then ground plant samples were kept in polyethylene bags for the purpose of testing the Ni, Cu, Pb, and Cr content in the plant root and shoot biomasses.

Table 2. Experimental treatments: Application and rate of MgO-modified biochars in the pot experiment.

Code	Treatment Description
T1= Control	1 kg soil
T2= TWMgO-MBC 0.5%	1 kg soil + Tea waste MgO-modified biochar 0.5%
T3= TWMgO-MBC 1%	1 kg soil + Tea waste MgO-modified biochar 1%
T4= WSMgO-MBC 0.5%	1 kg soil + Wood shave MgO-modified biochar 0.5%
T5= WSMgO-MBC 1%	1 kg soil + Wood shave MgO-modified biochar 1%
T6= WCMgO-MBC 0.5%	1 kg soil + Water chestnut MgO-modified biochar 0.5%
T7= WCMgO-MBC 1%	1 kg soil + Water chestnut MgO-modified biochar 1%
T8= PPMgO-MBC 0.5%	1 kg soil + Pomegranate peel MgO-modified biochar 0.5%
T9= PPMgO-MBC 1%	1 kg soil + Pomegranate peel MgO-modified biochar 1%

2.5. Analysis of Soils and MgO-Modified Biochars

Soil pH and electrical conductivity (EC) were determined by a 1:2 H_2O ratio for polluted soils, and a 1:10 H_2O ratio was used for MgO-modified biochars [47]. The organic matter content in both polluted soils and MgO-modified biochars was tested through the Walkley–Black titration method, as outlined by [48]. The cation exchange capacity in both polluted soils and MgO-modified biochars was quantified using the USEPA Method 9080 according to [49]. The lime $CaCO_3$ content in both polluted soils and MgO-modified biochars was determined through an acid neutralization procedure, followed by [44]. Total organic carbon in soils and MgO-modified biochars was tested using the wet oxidation method of Walkley and Black [48]. The dissolved organic carbon (DOC) concentration in both polluted soils and MgO-modified biochars was measured in ultrapure water in a 1:10 soil-to-water ratio using an automated TOC analyzer (Shimadzu TOC-L, Kyoto, Japan) according to [50]. The soil particle density and bulk density were determined, as described in [51]. The total concentration of Ni, Cu, Pb, and Cr in both polluted soils and MgO-modified biochars was determined by digesting the samples under mixed acid conditions (concentrated HCl-HNO_3-$HClO_4$, 5:5:1) using the protocol 3050B of the US Environmental Protection Agency [52].

2.6. Pearl Millet Plant Analysis

To test the Ni, Cu, Pb, and Cr in the root and shoot of the pearl millet plant, approximately 0.5 g of plant biomass was digested using nitric acid (HNO_3^-) and perchloric acid ($HClO_4^-$). The mixture was analyzed using an Inductively Coupled Plasma mass spectrometer (ICP-MS) with a ratio of 4:1 (ELAN DRC-e, Perkin Elmer SCIEX, Shelton, CT, USA) according to [53,54].

2.7. Statistical analysis

The experiment was carried out in triplicate. The data were subjected to statistical analysis using the Statistix 8.1 software package to assess the one-way analysis of variance (ANOVA) of each studied parameter via HSD at ($p < 0.05$). All the graphs were generated using Origin Pro 8.5 Version. Redundancy analysis was performed to assess the correlation among the studied parameters.

3. Results and Discussion

3.1. Effect of MgO-Modified Biochars on Pearl Millet Fresh and Dry Biomasses

The application of MgO-modified biochars was found to significantly ($p < 0.05$) increase the fresh and dry biomasses (shoot and root) of pearl millet grown in stone crushing and mining-polluted soil. Furthermore, the greatest fresh biomass was observed at 45.04 and 37.5% with the application of TWMgO-MBC 1% in stone crushing and mining-polluted soil (Figure 1a,b). The application of TWMgO-MBC 1% as an amendment significantly increased the dry biomass of pearl millet, with values of 31.29 and 26.02% in stone crushing and mining-polluted soil, respectively, in comparison with the control treatment (Figure 1c,d). These results indicate that TWMgO-MBC is highly effective in increasing the fresh and dry biomasses of pearl millet. The primary mechanism underlying this effect is the enhancement of soil organic matter (SOM) and cation exchange capacity (CEC), which, in turn, may facilitate the dissolution of nutrients and contribute to the growth of plant biomass in the soil. Lu et al. [38] were the first to apply magnetic biochars for the remediation of polluted soil. They observed an increase in rice plant growth of 32% with the addition of magnetic poultry litter biochar at 300 and 500 °C. Furthermore, they demonstrated that surface modification through magnetization can have a substantial influence on plant yield. In comparison with the control treatment, the EC level was reduced by a range of 2.14 to 1.39 dS/cm with the application of PPMgO-MBC 1% in stone-crushing-polluted soil. Similarly, the EC level in mining-polluted soil was reduced from 2.89 to 1.70 dS/cm with the addition of WCMgO-MBC 1% in comparison with other amendments (Figure 1e,f). Ibraheem et al. [55] found that the combination of biochar and municipal solid waste compost can enhance soil structure and CEC, leading to a decrease in electrical conductivity in saline soil. Nevertheless, Wang et al. [56] demonstrated that the electrical conductivity (EC) of soil was increased following the application of MgO-treated corn straw biochar at a dosage of 1.5%; however, this resulted in alterations to the microbial dynamics within the soil. The authors observed that MgO-modified biochar has a negative impact on the soil microbial population, which was attributed to the release of weakly bound nutrients and soluble salts in the soil medium. Additionally, Kane et al. [57] reported that the physical and chemical mechanisms affecting the electrical conductivity of lignin-derived biochar are influenced by the biochar oxygen content and particle size. They also noted that lignin feedstock may increase biochar electrical conductivity.

3.2. Effect of MgO-Modified Biochars on Soil Chemical Properties

The pH value in stone crushing and mining-polluted soil was increased from 7.22 to 8.45 and 7.33 to 8.13, respectively, with the application of WSMgO-MBC 1% in comparison with other treatments (Figure 2a,b). The maximum cation exchange capacity (CEC) in stone-crushing-polluted soil was increased by 84.17% with the application of WSMgO-MBC 1%, and similarly, the CEC in mining-polluted soil was increased by up to 79.62% with the addition of WCMgO-MBC 1% in comparison with the control treatment (Figure 2c,d). The proportion of calcium carbonate ($CaCO_3$) was increased by 42.19 and 66.01% with the application of WSMgO-MBC 1% in stone-crushing-polluted soil and mining-polluted soil, respectively, as compared with the control treatment (Figure 2e,f). Zheng et al. [58] observed an increase in CEC in multimetal-polluted soil following the application of rice husk biochar. Nkoh et al. [59] reported that biochar possesses a negative charge due to the presence of organic functional groups (e.g., -OH, -COOH), which results in a high cation exchange capacity. This is attributed to the biochar's high cation ions, large surface area, and porosity. Ghassemi-Golezani and Rahimzadeh [60] stated that biochar has the potential to increase soil pH and CEC. They further revealed that modified biochar can greatly enhance the specific surface area, functional groups, and cation exchange capacity as compared with unmodified biochar. Saleem et al. [3] found that the application of thiourea-modified biochar in heavy-metal-polluted soil resulted in an increase in the soil's $CaCO_3$ content.

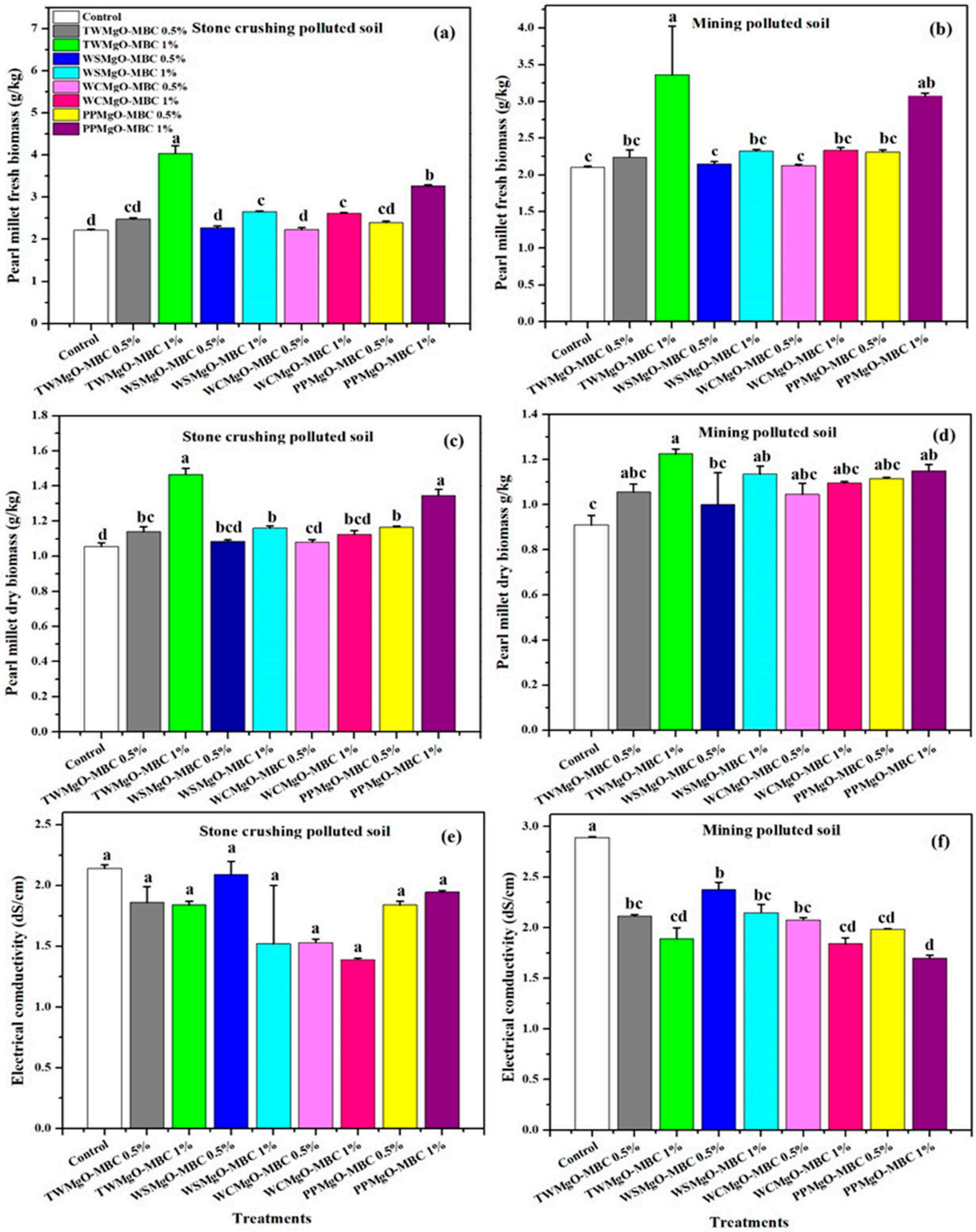

Figure 1. Effect of MgO-modified biochars on pearl millet fresh biomass in stone-crushing-polluted soil (**a**), pearl millet fresh biomass in mining-polluted soil (**b**), pearl millet dry biomass in stone-crushing-polluted soil (**c**), pearl millet dry biomass in mining-polluted soil (**d**), EC in stone-crushing-polluted soil (**e**), and EC in mining-polluted soil (**f**). The error bars indicate the standard deviation of the mean (n = 3). Values in a given column that share the same letter are not significantly different ($p < 0.05$) according to the Tukey test.

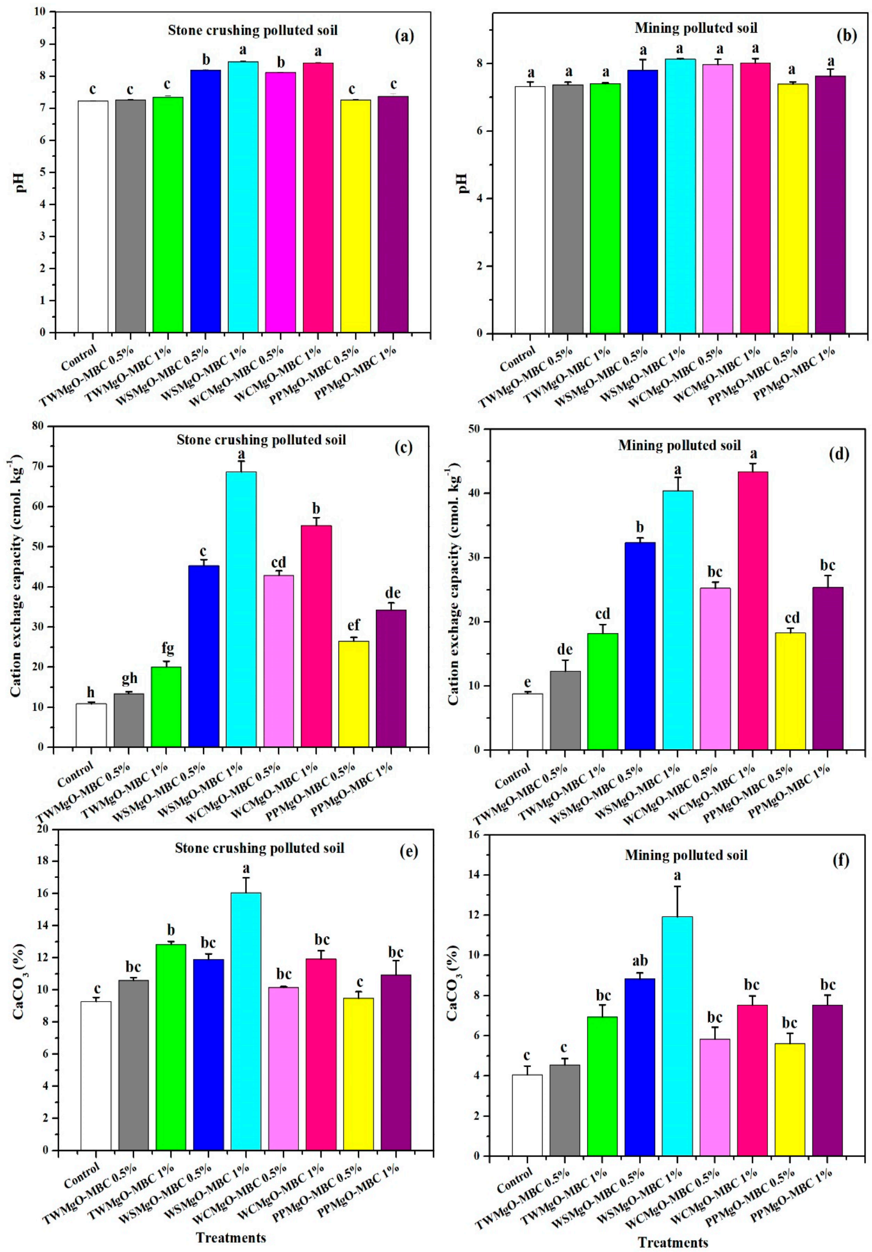

Figure 2. Effect of MgO-modified biochars on pH in stone-crushing-polluted soil (**a**), pH in mining-polluted soil (**b**), CEC in stone-crushing-polluted soil (**c**), CEC in mining-polluted soil (**d**), $CaCO_3$ in stone-crushing-polluted soil (**e**), and $CaCO_3$ in mining-polluted soil (**f**). The error bars indicate the standard deviation of the mean (n = 3). Values in a given column that share the same letter are not significantly different ($p < 0.05$) according to the Tukey test.

The highest dissolved organic carbon (DOC) in stone crushing and mining-polluted soil was increased by 38.21 and 53.6%, respectively, with the addition of TWMgO-MBC 1% in comparison with the control treatment (Figure 3a,b). The higher soil organic matter (SOM) in stone-crushing-polluted soil was increased by 34.16% with the application of TWMgO-MBC 1%. Moreover, the maximum SOM content in mining-polluted soil was increased by 41.02% with the addition of PPMgO-MBC 1%, as compared with the other treatments (Figure 3c,d). The highest particle density (PD) in stone crushing and mining-polluted soil was reduced from 2.35 to 2.18 and 2.53 to 2.15 g/cm^3, respectively, as compared with the control treatment (Figure 3e,f). The reduction in soil bulk density (BD) was from 1.41 to 1.15 g/cm^3 with the application of TWMgO-MBC 1% in stone-crushing-polluted soil, while the maximum reduction in BD in mining-polluted soil was from 1.49 to 1.16 g/cm^3

with the addition of PPMgO-MBC 1%, as compared with the control treatment (Figure 3g,h). These results indicate that biochar has a lower bulk density of 0.6 g/cm^3, which reduces the BD and PD in soil through the mixing and/or dilution effects of MgO-modified biochars at higher dosages (1%). Sun et al. [43] observed an increase in organic matter in soil with the addition of chestnut shell-derived biochar (CsBC300) in alkaline polluted soil. Wang et al. [56] noted that the soil pH and DOC content increased as a consequence of Pb transformation with an elevated dose of MgO-treated corn straw biochar, rising from 0.5 to 1.5%. Toková et al. [61] demonstrated that soil bulk density and particle density were reduced with the application of biochar at 10 and 20 t ha^{-1}.

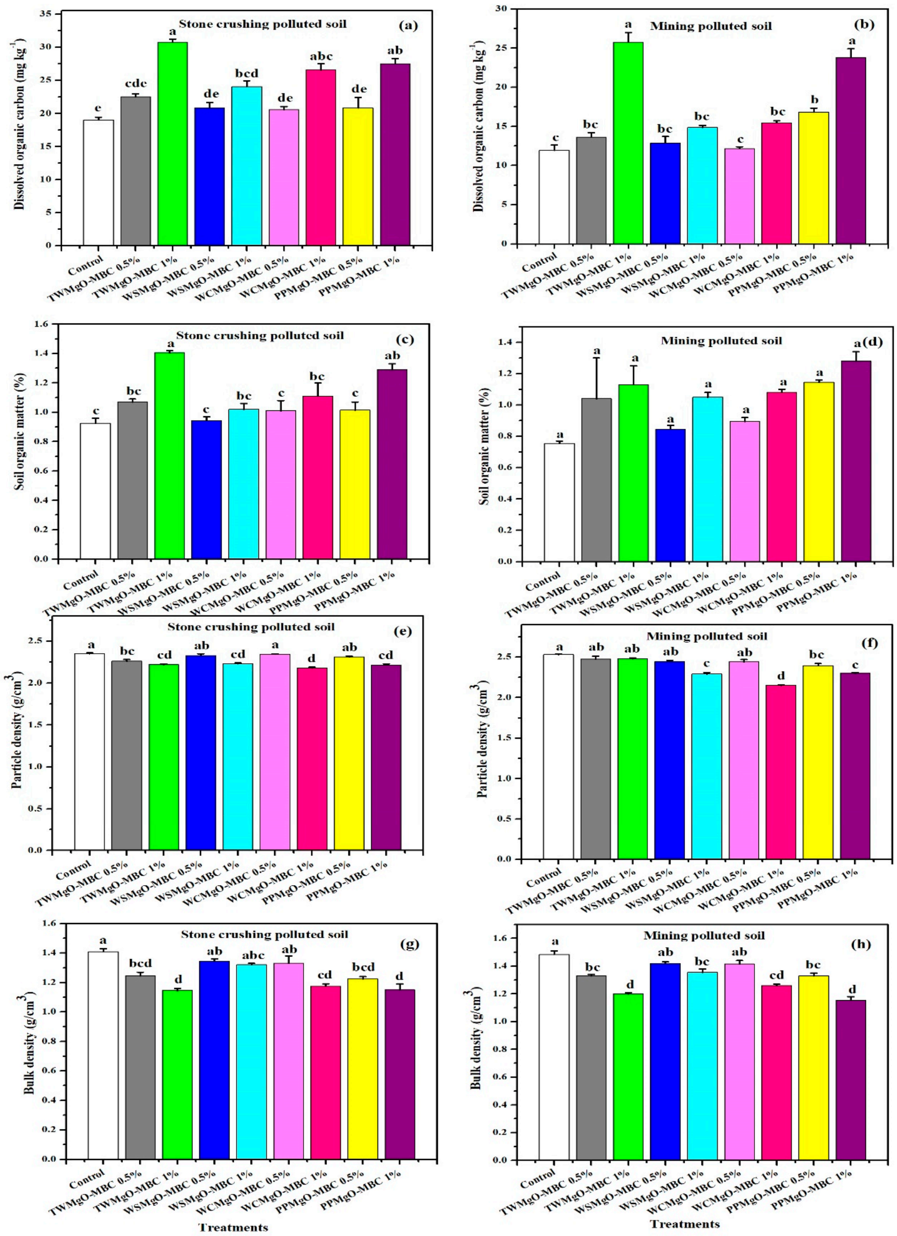

Figure 3. Effect of MgO-modified biochars on dissolved organic carbon in stone-crushing-polluted soil (**a**), dissolved organic carbon in mining-polluted soil (**b**), soil organic matter in stone-crushing-polluted soil (**c**), soil organic matter in mining-polluted soil (**d**), particle density in stone-crushing-polluted soil (**e**), particle density in mining-polluted soil (**f**), bulk density in stone-crushing-polluted soil (**g**), and bulk density in mining-polluted soil (**h**). The error bars indicate the standard deviation of the mean (n = 3). Values in a given column that share the same letter are not significantly different ($p < 0.05$) according to the Tukey test.

3.3. Effect of MgO-Modified Biochars on the Immobilization of Total Ni, Cu, Pb, and Cr in Soils

The highest Ni immobilization in stone crushing and mining-polluted soil was observed at 70.71 and 76.67% with the application of WSMgO-MBC 1% in comparison with the control treatment (Figure 4a,b). The stabilization of Cu was recorded at 59.73% with WSMgO-MBC 1% in stone-crushing-polluted soil and 73.45% with WCMgO-MBC 1% in mining-polluted soil, compared with treatment without modification (Figure 4c,d). The greatest Pb immobilization in stone crushing and mining-polluted soil was observed at 76.78 and 74.21% with the addition of WSMgO-MBC 1% compared with the control treatment (Figure 4e,f). The WCMgO-MBC 1% treatment was found to be an efficacious soil amendment in immobilizing Cr, with a stabilization rate of up to 70.55% compared with the control. The greatest stabilization of Cr in mining-polluted soil was determined in the treatment amended with WSMgO-MBC 1% (47.95%) (Figure 4g,h). These results indicate that WSMgO-MBC 1% and WCMgO-MBC 1% are highly effective soil amendments for immobilizing Ni, Cu, Pb, and Cr in stone crushing and mining-polluted soil. This was due to an increase in soil pH, CEC, SOM, DOC, and a reduction in particle density and bulk density. Lu et al. [38] discovered that the maximum removal of Pb and Cu in soil was achieved with the addition of magnetic eucalyptus biochar (MEB) and magnetic poultry litter MPLB at 300 and 500 °C compared with the control treatment. Shen et al. [39] observed a reduction in Pb levels in soil following the application of MgO-coated corncob biochar (MCB) as compared with corncob biochar. Furthermore, the results indicate that the main mechanism underlying Pb may be the cation–π interaction, precipitation, and a high surface area in soil with the application of MCB biochar. Liu et al. [62] found that the incorporation of modified coconut shell biochar reduced the Ni concentration in soil. Liu et al. [63] applied Fe-rice-husk-derived biochar to polluted soil, which resulted in a reduction in hexavalent–chromium by up to 81% in comparison with the control soil. Leng et al. [64] stated that modified biochar can be considered a soil conditioner with the potential to remediate multimetal-polluted soils by improving soil properties. Liang et al. [65] reviewed the main mechanisms underlying the remediation of metals in polluted soil. These include ion exchange, heavy metals with Ca^{2+}, Mg^{2+}, and other cations associated with biochar, adsorption, co-precipitation, electrostatic attraction, internal compounds with humic substances, and the complexing function of oxygen-efficient groups and π electrons.

3.4. Effect of MgO-Modified Biochars on the Uptake of Ni, Cu, Pb, and Cr by Plant Shoot

The uptake of Ni, Cu, Pb, and Cr in the shoots of pearl millet plants was found to be reduced with the application of MgO-modified biochars, in comparison with the control treatment. However, the greatest reduction in Ni uptake in the shoots of pearl millet was observed at 61.51 and 78.43%, respectively, with the application of WSMgO-MBC 1% in stone crushing and mining-polluted soil, as compared with the control treatment (Figure 5a,b). The Cu absorption in the shoots of pearl millet decreased by 59.33 and 75.06% with the addition of WSMgO-MBC 1% in stone crushing and mining-polluted soil (Figure 5c,d). The accumulation of Pb in the shoots of pearl millet was reduced by 81.37% with the application of WSMgO-MBC 1% in stone-crushing-polluted soil. Furthermore, the greatest reduction in Pb accumulation in the shoots of pearl millet was noted in the WCMgO-MBC 1% treatment in mining-polluted soil, with a reduction of 90.81% compared with the nonamended control (Figure 5e,f). The concentration of Cr in the shoots of pearl millet was reduced by 82.15% in stone-crushing-polluted soil when PPMgO-MBC 1% was added. Compared with the control treatment, the greatest reduction in Cr content in the shoots of pearl millet (85.71%) was observed when WSMgO-MBC 1% was added to mining-polluted soil (Figure 5g,h). These results reveal that the contents of Ni and Cu in the shoots of pearl millet were reduced with the application of WSMgO-MBC 1%, Pb with WSMgO-MBC 1% and WCMgO-MBC 1%, and Cr with PPMgO-MBC 1% and WSMgO-MBC 1% in stone crushing and mining-polluted soil. Shahbaz et al. [66] observed reduced Ni concentration in the shoots of sunflower and maize, reaching up to 50 and 49%, respectively, following the application of Silver grass biochar produced at 350 °C.

Lu et al. [38] reported that Pb and Cu concentrations in the shoots of rice crops were reduced with the application of poultry litter biochar produced at 500 °C. Rajput et al. [67] discovered that the Cr concentration in the biomass of barley plant was reduced with the application of biochar. The main mechanisms underlying this reduction were identified as surface adsorption, exchange, surface complexation, and precipitation of heavy metals in polluted soil.

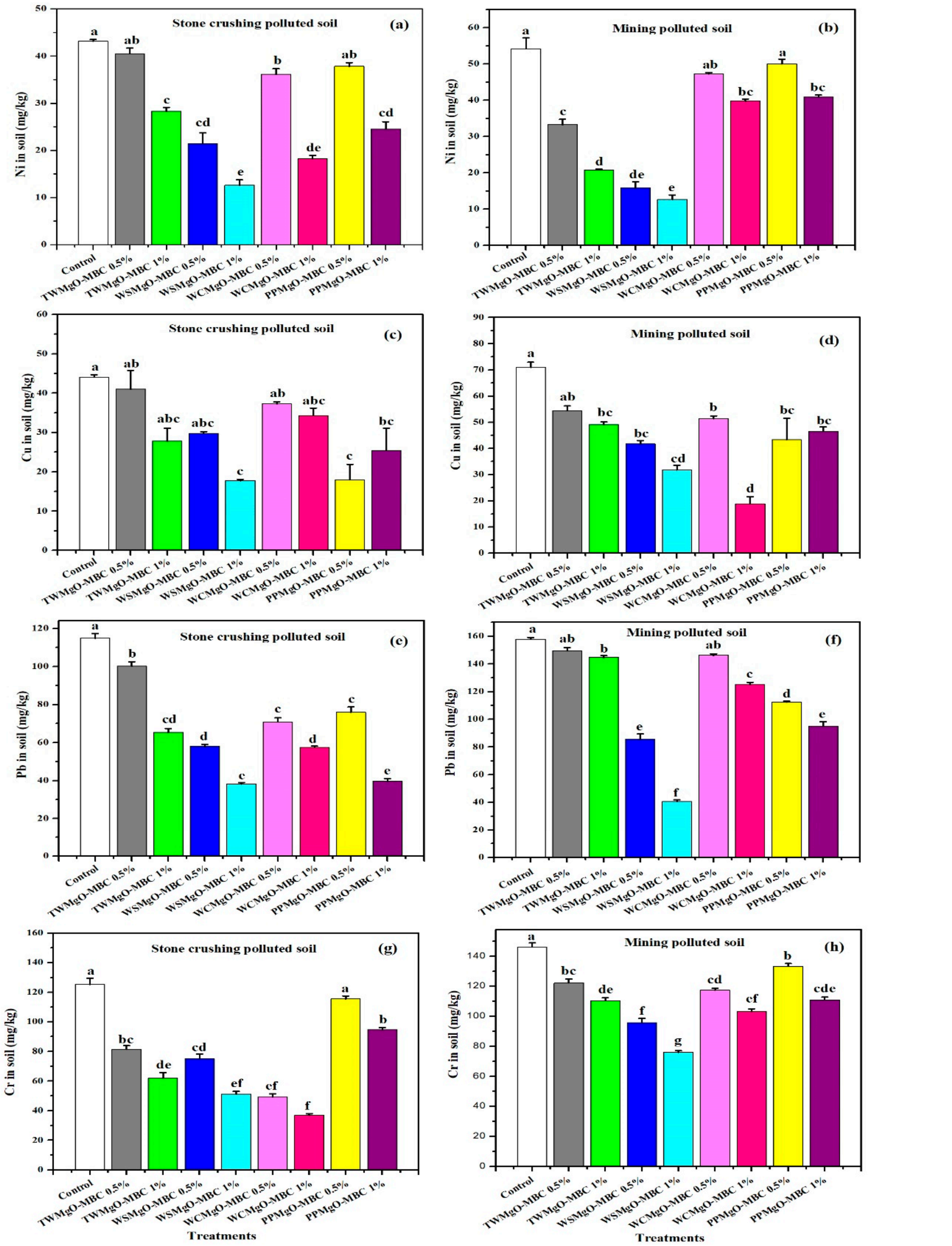

Figure 4. Effect of MgO-modified biochars on Ni in stone-crushing-polluted soil (**a**), Ni in mining-polluted soil (**b**), Cu in stone-crushing-polluted soil (**c**), Cu in mining-polluted soil (**d**), Pb in stone-crushing-polluted soil (**e**), Pb in mining-polluted soil (**f**), Cr in stone-crushing-polluted soil (**g**), and Cr in mining-polluted soil (**h**). The error bars indicate the standard deviation of the mean (n = 3). Values in a given column that share the same letter are not significantly different ($p < 0.05$) according to the Tukey test.

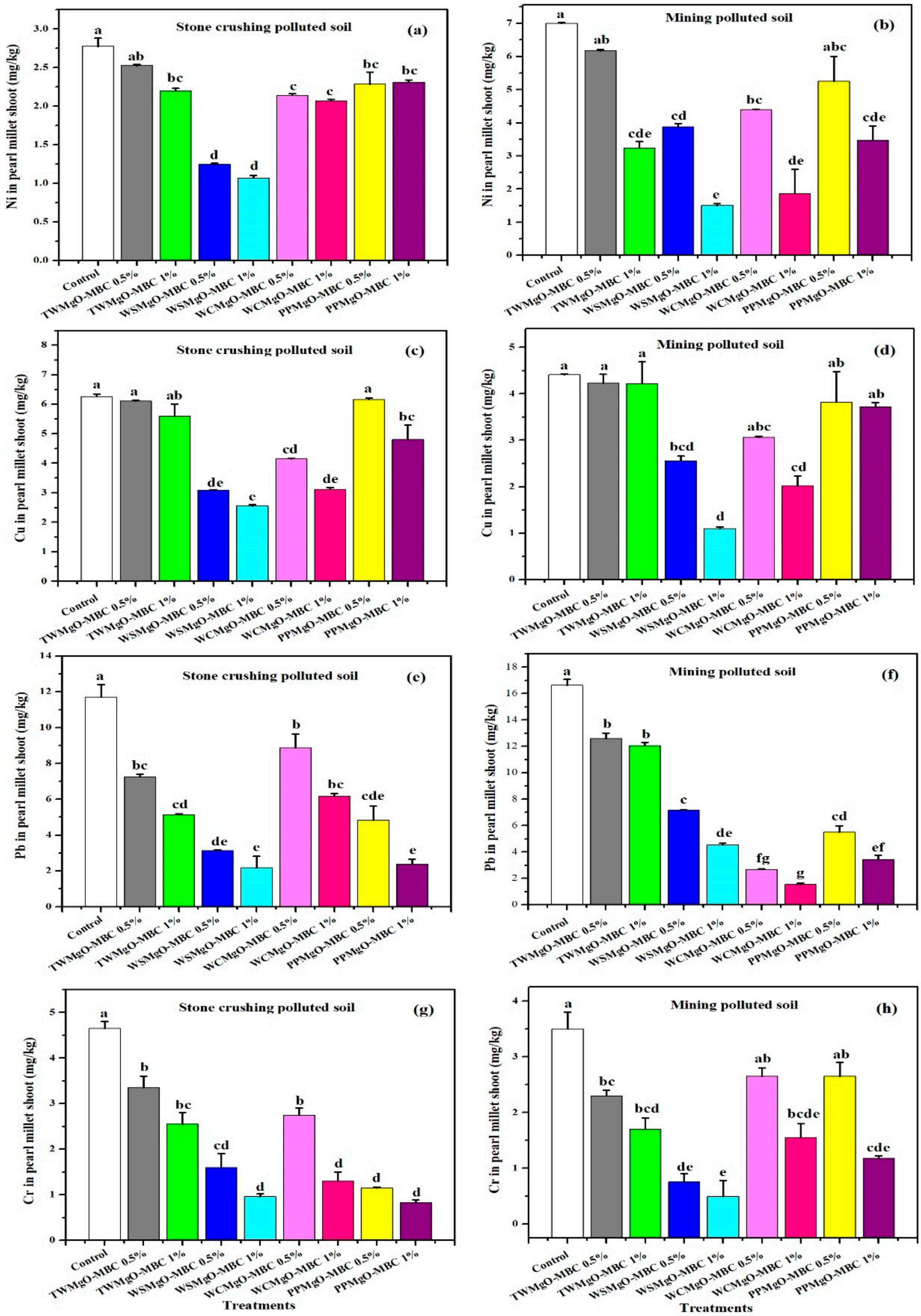

Figure 5. Effect of MgO-modified biochars on Ni uptake by plant shoot in stone-crushing-polluted soil (**a**), Ni uptake by plant shoot in mining-polluted soil (**b**), Cu uptake by plant shoot in stone-crushing-polluted soil (**c**), Cu uptake by plant shoot in mining-polluted soil (**d**), Pb uptake by plant shoot in stone-crushing-polluted soil (**e**), Pb uptake by plant shoot in mining-polluted soil (**f**), Cr uptake by plant shoot in stone-crushing-polluted soil (**g**), and Cr uptake by plant shoot in mining-polluted soil (**h**). The error bars indicate the standard deviation of the mean (n = 3). Values in a given column that share the same letter are not significantly different ($p < 0.05$) according to the Tukey test.

3.5. Effect of MgO-Modified Biochars on the Uptake of Ni, Cu, Pb, and Cr by Plant Root

The accumulation of Ni in the root of pearl millet was reduced by 57.61% and 77.81% with the application of WSMgO-MBC 1% in the stone crushing and mining-polluted soil (Figure 6a,b). The greatest reduction in Cu in the root of pearl millet was observed at 68.09% with the addition of WCMgO-MBC 1% in stone-crushing-polluted soil (Figure 6c). Similarly, the reduction in Cu in the root of pearl millet was observed to reach 42.61% with the application of TWMgO-MBC 1%, as compared with the control treatment, in mining-polluted soil (Figure 6d). The absorption of Pb in the root of pearl millet was found to be significantly reduced, with an absorption rate of up to 77.39% in stone-crushing-polluted soil, when WSMgO-MBC 1% was applied (Figure 6e). In comparison with the control treatment, the addition of WCMgO-MBC 1% to mining-polluted soil resulted in a maximum reduction in Pb in the root of pearl millet of 84.03% (Figure 6f). Similarly, the application of WSMgO-MBC 1% to stone-crushing-polluted soil led to a reduction in Cr concentration in the root of pearl millet of 80.31% (Figure 6g). The greatest reduction in Cr in the root of pearl millet was observed to be 88.73% with the application of WCMgO-MBC 1% in mining-polluted soil, as compared with the control treatment (Figure 6h). The results show that the greatest reduction in Ni in the root of pearl millet was achieved with the application of WSMgO-MBC 1%, Cu with WCMgO-MBC 1% and TWMgO-MBC 1%, Pb with WSMgO-MBC 1% and WCMgO-MBC 1%, and Cr with WSMgO-MBC 1% and WCMgO-MBC 1%. It is possible that the observed increase in soil pH, DOC, $CaCO_3$, and CEC may be responsible for these reductions in the uptake of heavy metals in polluted rhizosphere soils. Our findings align with those of Lu et al. [38], who observed a decline in Cu content in rice roots following the application of poultry litter biochar produced at 500 °C. Similarly, Rehman et al. [68] examined the impact of rice-straw-derived biochar (300 °C) and found a 50% reduction in Cu in the roots of the Ramie plant relative to the control treatment. Additionally, Sehrish et al. [69] reported that Cr uptake by the shoot of spinach reached 49% with the application of poultry litter biochar produced at 300 °C. Furthermore, Ahmad et al. [70] observed a reduction in Pb content in the root of lettuce (*Lactuca sativa*) with the application of lead chicken manure at 400 °C. Huang et al. [71] found that cattle manure biochar produced at 350 °C and applied at a rate of 3% has the potential to reduce Cu and Pb in the root of lettuce (*Lactuca sativa*). Ali et al. [72] revealed that rice-straw-derived biochar as an amendment significantly reduced Ni in the root of maize plants. Ghandali et al. [73] demonstrated that the uptake of Pb and Ni in the root of ryegrass was significantly greater when ZnO and MnO_2 nanoparticle-modified biochar was applied than when a control was used.

3.6. Redundancy Analysis among the Parameters under Investigation

A redundancy analysis was conducted on a number of variables, including fresh biomass, dry biomass, electrical conductivity (EC), soil pH, cation exchange capacity (CEC), organic matter (OM), dissolved organic carbon (DOC), calcium carbonate ($CaCO_3$), particle density (PD), bulk density (BD), total Ni, Cu, Pb, and Cr contents in soil, Ni, Cu, Pb, and Cr contents in the shoots and roots of pearl millet grown in stone crushing and mining-polluted soil (Figure 7). The first axis, RDA 1, explained 65.21% of the variance, and the second axis, RDA 2, explained 16.73% of the variance. The results indicate that soil organic matter and dissolved organic carbon were positively correlated with pearl millet fresh and dry biomasses but negatively associated with particle density and bulk density. Furthermore, soil pH, cation exchange capacity, and calcium carbonate were negatively correlated with Cu, Pb, and Cr in soil, and pearl millet shoot and root biomasses in stone-crushing-polluted soil. The first axis, RDA 1, explained 59.73% of the variance, and the second axis, RDA 2, explained 16.87% of the variance. The results show that soil organic matter and dissolved organic carbon were positively correlated with plant fresh and dry biomasses. However, a negative correlation was observed between soil organic matter and dissolved organic carbon and electrical conductivity, particle density, and bulk density. It was observed that soil pH, cation exchange capacity, and calcium carbonate were negatively correlated with Cu, Pb, and Cr in soil, as well as with pearl millet shoot and root biomasses in mining-polluted soil. Saleem et al. [74] identified a significant correlation between Cr and several soil chemical parameters, including pH, EC, CEC, and OM. Ghassemi-Golezani and Rahimzadeh [60] reported that there is a positive association between soil pH and CEC, as biochar has the potential to enhance soil CEC by increasing soil pH. Lahori et al. [75] observed a positive correlation between soil organic matter and cation exchange capacity, while soil pH exhibited a negative correlation with Cu in soil and Cu in mustard shoots and roots.

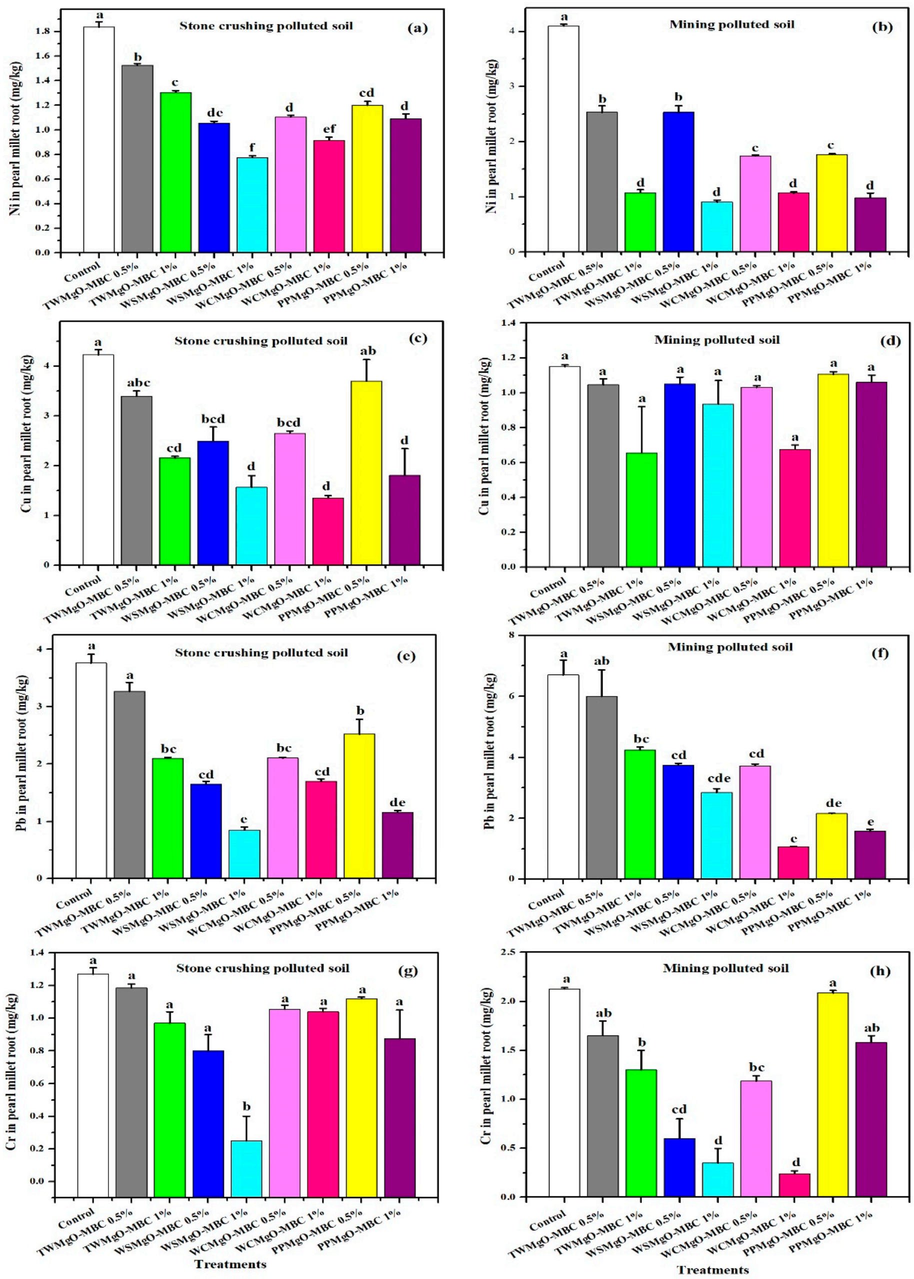

Figure 6. Effect of MgO-modified biochars on Ni uptake by plant root in stone-crushing-polluted soil (**a**), Ni uptake by plant root in mining-polluted soil (**b**), Cu uptake by plant root in stone-crushing-polluted soil (**c**), Cu uptake by plant root in mining-polluted soil (**d**), Pb uptake by plant root in stone-crushing-polluted soil (**e**), Pb uptake by plant root in mining-polluted soil (**f**), Cr uptake by plant root in stone-crushing-polluted soil (**g**), and Cr uptake by plant root in mining-polluted soil (**h**). The error bars indicate the standard deviation of the mean (n = 3). Values in a given column that share the same letter are not significantly different ($p < 0.05$) according to the Tukey test.

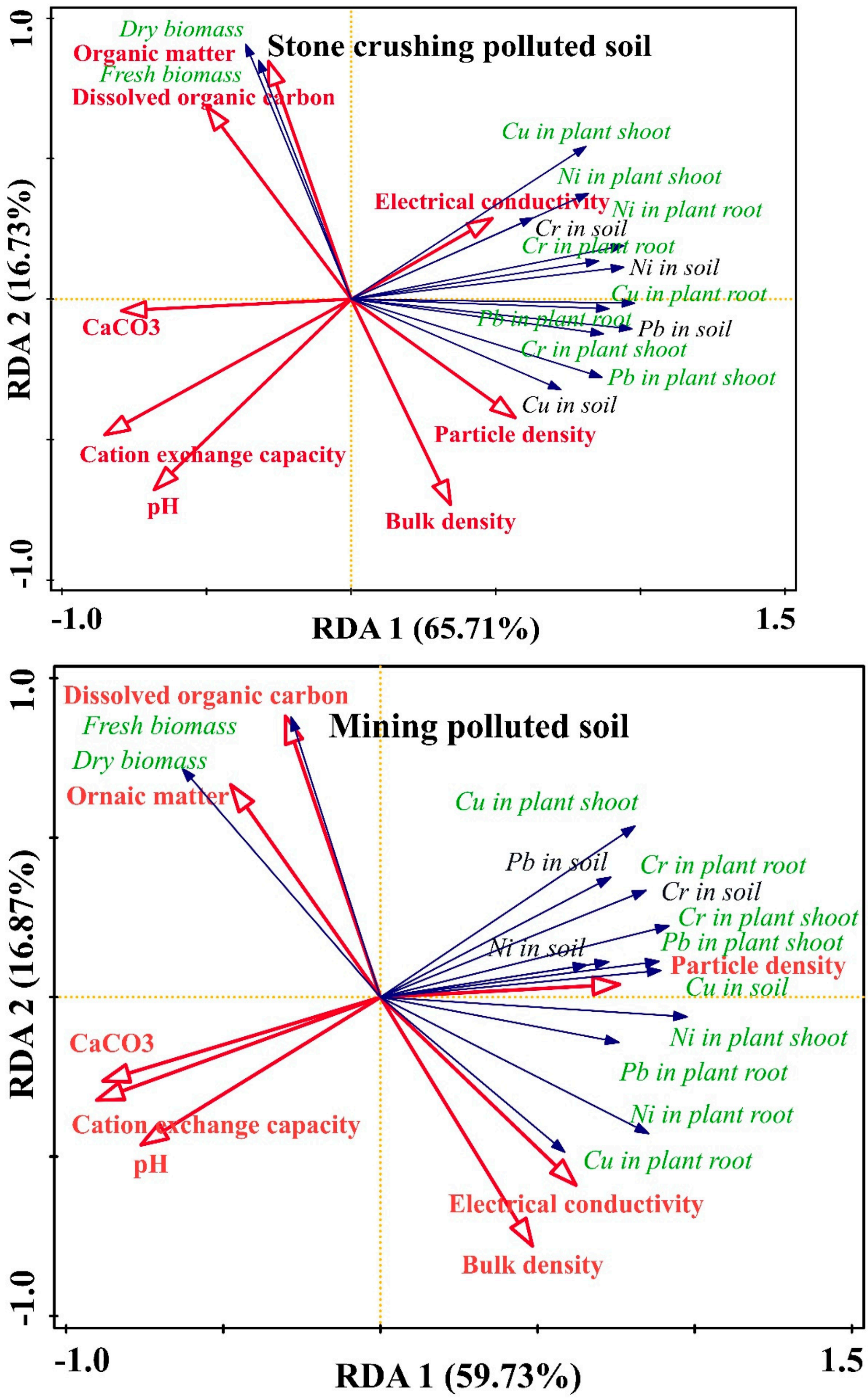

Figure 7. Redundancy analysis among fresh biomass, dry biomass, electrical conductivity (EC), soil pH, cation exchange capacity (CEC), organic matter (OM), dissolved organic carbon (DOC), calcium carbonate ($CaCO_3$), particle density (PD), bulk density (BD), total Ni, Cu, Pb, and Cr contents in soil, Ni, Cu, Pb, and Cr contents in the shoots and roots of pearl millet grown in stone crushing and mining-polluted soil after the application of MgO-modified biochars.

4. Conclusions

The potential of MgO-modified biochars for the stabilization of Ni, Cu, Pb, and Cr in stone crushing and mining-polluted soil was investigated. The findings of the present study indicated that MgO-modified biochars as amendments can immobilize Ni, Cu, Pb, and Cr in polluted soils and reduce their uptake by the pearl millet plant. The application of tea waste MgO-modified biochar at 1% demonstrated a high potential for increasing fresh and dry biomasses of pearl millet. The application of wood shavings MgO-modified biochar at a 1% dose and water chestnut MgO-modified biochar at a 1% dose significantly immobilized Ni, Cu, Pb, and Cr in stone crushing and mining-polluted soil. The uptake of Ni, Cu, Pb, and Cr by the roots and shoots of pearl millet was observed with the wood shavings MgO-modified biochar 1%, water chestnut MgO-modified biochar 1%, and pomegranate peel MgO-modified biochar 1% treatments, as compared with the control soil. In comparison with the control soil, the application of amendments resulted in an increase in pH, CEC, $CaCO_3$, DOC, and OM, while a reduction was observed in EC, PD, and BD. These observations suggest that the amendments may have contributed to the immobilization of heavy metals in polluted soils. The application of MgO-modified biochars at a rate of 1% has the potential to remediate heavy metals in stone crushing and mining-polluted soils. This study provides a clear roadmap for the safe cultivation of crops in polluted soil and indicates findings that are useful for the farming community, researchers, and scientists in the field of environmental science and technology. Future studies should be conducted to assess the impact of MgO-modified biochars on soil microbial activity, soil fertility, soil salinity, gene sequences, carbon sequestration, plant physiology, and the immobilization of multimetal in agriculture-polluted soils under field conditions. This will help to reduce the heavy metal stress in the soil environment, thereby ensuring food safety in Pakistan.

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