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Novel Fuller Earth, Rock Phosphate, and Biochar for Phytomanagement of Toxic Metals in Polluted Soils

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Abstract: The present study was aimed to assess the efficacy of individual and combined effects of novel fuller earth, rock phosphate, and biochar (grapefruit peel) at 1% dosage on maize plant growth, soil chemical properties anduptake of toxic metals (TMs), such as Cu, Zn, Fe, and Cd, by maize plant sown in Korangi (district of Karachi, Pakistan) heavily polluted and Korangi less polluted (K-HP and K-LP) soils. The obtained results indicate that the dry biomass of maize crop increased by 14.13% with combined (FE1% + GBC1%) on K-HP soil and 18.24% with combined (FE 1% + GBC 1%) effects on K-LP soil. The maximum immobilization of Cu, Zn, Fe, and Cd was observed by 36% with GBC1%, 11.90% with FE1%, 98.97% with combined RP1% + GBC1%, 51.9% with FE1% + GBC1% for K-HP, 11.90% with FE1%, 28.6% with FE1%, 22.22% with RP1% + GBC1%, and 57.05% with FE 1% + GBC 1% for K-LP soil. After the addition of proposed substances, modification of soil OM, SOC, TOC, and pH level appeared this lead to the changes in the phyto-availability of Cu, Zn, Fe, and Cd in maize plant. It was concluded that the application of individual and combined effects of novel fuller earth, rock phosphate, and biochar (grapefruit peel) have potential to stabilize pollutants from multi-metal polluted soils for safe crop production.

Keywords: novel fuller earth; rock phosphate; biochar; immobilization; toxic metals; maize

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1. Introduction

Global industrialization and human activities, such as smelting, mining ores, modern agriculture practices, and waste disposal methods rapidly pollute soils with toxic metals (TMs) [1,2]. Soil contamination by TMs had been a global task for food safety, and environment [3,4], because TMs in soil do no degrade into other forms rapidly, and their persistence in the environment could affect agriculture productivity and the soil ecosystem as a result it may possess a serious health problems for all living organisms [5]. Nevertheless, appearances of health problems, such as nausea, vomiting, epigastric pain, lethargy, and fatigue will occur with enormous Zn intakes; these risky elements negatively affected not only human beings but also plant development [6,7]. Although the cleanup of TM soils is very necessary, many methods and techniques were adopted to remove TMs from factory-polluted soil, but came up with many disadvantages. The implementation of most conventional reclamation approaches e.g., phytoremediation, land filling, electro-kinetic, surface capping, vitrification, and soil washing/flushing, are non-feasible on a large scale, ecologically disturbing, and too expensive [8].

Amongst these technologies, in situ fixation of TMs is thought to be the best opportunity and a robust technology for restoration of TM-polluted sites [9]. The principal mechanism of TM fixation in soil with additional BC depends on (ad)sorption, pH, CEC, electrostatic attraction, temperature, redox potential, and precipitation [10,11]. Furthermore, soil additives would have a high immobilizing capability, be easily available in the market, low in cost, and eco-friendly for restoration of top polluted sites [12]. Indeed, an immobilizing agent might be effective at immobilizing one toxin, however, may increase the solubility of another TM [13]. In the previous study, Naiya et al. [14] used the fuller's earth in aqueous solutions for reducing Pb (II) solubility. Mohammed et al. [15] applied the locally available red earth and black cotton soils in retaining Cd^{2+} and Ni^{2+} from aqueous medium.

Furthermore, phosphate compounds are known to be active in the fixation of lead, cadmium, and zinc [16]. Precipitation of metal phosphates is deliberated as the main process behind the fixation [17]. For example, Cao et al. [18] confirmed that the rock phosphate (RP) declined bio-available Pb through the development of pyromorphite-like minerals. Biochar (BC) is a carbon-rich material acquired from pyrolysis, the thermo-chemical conversion of feedstock in the absence of or under limited O_2 [19]. Furthermore, BC can be considered as the robust and best approach for reducing TM concentrations from contaminated soils, because structurally it is macro/mirco-porous and has a large surface area [20]. Over the last few years, former studies described that different BC has great potential to reduce TMs in soil, as well as absorption by plants, because of its economically feasible remediation option [20,21]. The production of biomass produces a large amount of waste, therefore, feedstock can be measured as a good managing method, and treatment of large quantities of biological waste, viz., household solids and semi-solid waste, agricultural crop waste material, food waste, animal manure, and industrial waste material can be considered [22]. Mohan et al. [23] revealed that biochar (BC) as a soil amendment can be considered as cost-effective and eco-friendly biotechnology that has the potential to stabilize organic and inorganic pollutants in contaminated soils. It has micro-pores, which are also essential for the degradation of soluble organic matter and decreased microbe development, thus promoting the solution of biological pollutants in soils [24].

Moghal et al. [25] assessed the response of chemically modified soils in the sorption of chromium and mercury from aqueous solutions. It was observed that remediation costs using BC were several times lower than standard approaches, such as physical treatment, biological reclamation, and phytoremediation [26]. The unofficial disposal of a huge quality of fruit waste material produced each day in the mega city Karachi, may cause economic and environmental issues; it is recommended that the conversion of fruit peel waste into BC through pyrolysis might be used as an effective soil amendment [27]. Zhang et al. [28] applied grapefruit peel-made biochar as an amendment to enhance the removal of Cu(II) from aqueous solution. Anae et al. (2021) [11] revealed that BC engineered with hydrogel, digestate, and microorganisms for wider bioremediation options for clean-up of polluted soils [29]. Based on the stated lack of data and research gap, it is vital to build a novel understanding of the following scientific questions: (1) What is the impact of fuller earth, rock phosphate, and grapefruit peel made bio-char on maize biomass, soil chemical properties, stability, and uptake of Cu, Zn, Fe, and Zn in maize plant? (2) What is the individual and combined application of feasible amendments on plant growth and stability of TMs from multi-metal polluted soils? Up-to-date, no any research work has been done to explore the restoration of Cu, Zn, Fe, and Cd amended alone and with the combined application of fuller earth, rock phosphate, and grapefruit peel-made BC in factory-polluted areas of Korangi, Karachi. These areas are gradually polluting due to anthropogenic activities, and it is very imperative to remediate the TM load from factory-contaminated soil of Korangi, Karachi with the application of feasible and low cost immobilizing agents. Therefore, the main objective of the present study was to assess the impact of novel fuller earth, rock phosphate, and grapefruit peel-made biochar alone and in combined treatments on maize biomass, phytomanagement of Cu, Zn, Fe, and Zn, and chemical properties in K-HP and K-LP polluted soils. Our scientific hypothesis was that the application of novel fuller earth, rock phosphate, and grapefruit peel-made biochar alone and mixed may stabilize Cu, Zn, Fe, and Cd solubility in K-HP and K-LP soils for safe crop production.

2. Materials and Methods

2.1. Study Area, Soil Collection, and Characterization

In the present study, two contaminated soils, such as Korangi heavily polluted (K-HP), and Korangi less polluted (K-LP) soils were collected from Korangi District, which is located in Sindh, Pakistan. The Korangi Industrial Area is Pakistan's largest industrial zone. It was situated between latitude 24.8345° N and longitude 67.1213° E. Furthermore, K-HP was collected from close to the industrial site, whereas K-LP was collected an approximately 3 km from the industrial site. It was observed that, in the few decades since, many factories were established in this area, such as sugar mills, flour industries, oil refineries, plastic industries, pharmaceutical industries etc. The untreated effluent from these industry areas are gradually discharging in the in the soil medium, and as a result, polluting the soil with TMs and polluting the ground water. The map location of the studied area is indicated in (Figure 1). The contaminated soil samples were collected from the surface 0–15 cm at the depth from the Korangi Industrial Area. The samples were air-dried for 3 weeks at room temperature. Afterward, dried soil samples were ground to pass <2 mm mesh size for analysis. Both soils were alkaline in nature, while the electrical conductivity and water holding capacity of K-LP was higher than K-HP soil. K-HP was sandy clay and K-LP was sandy loam in textural class. K-LP was more dominant in OM, TOC, and SOC than K-HP soil. The total TM concentration was found higher in K-HP soil than in K-LP soil. The selected chemical properties of amendments revealed that the pH of GBC was higher than FE and RP, whereas the EC of FE was found to be greater than RP and GBC. The water holding capacity of GBC was higher as compared with FE and RP. Furthermore, the selected data regarding the physicochemical parameters of the two soils and amendments are indicated in (Table 1).

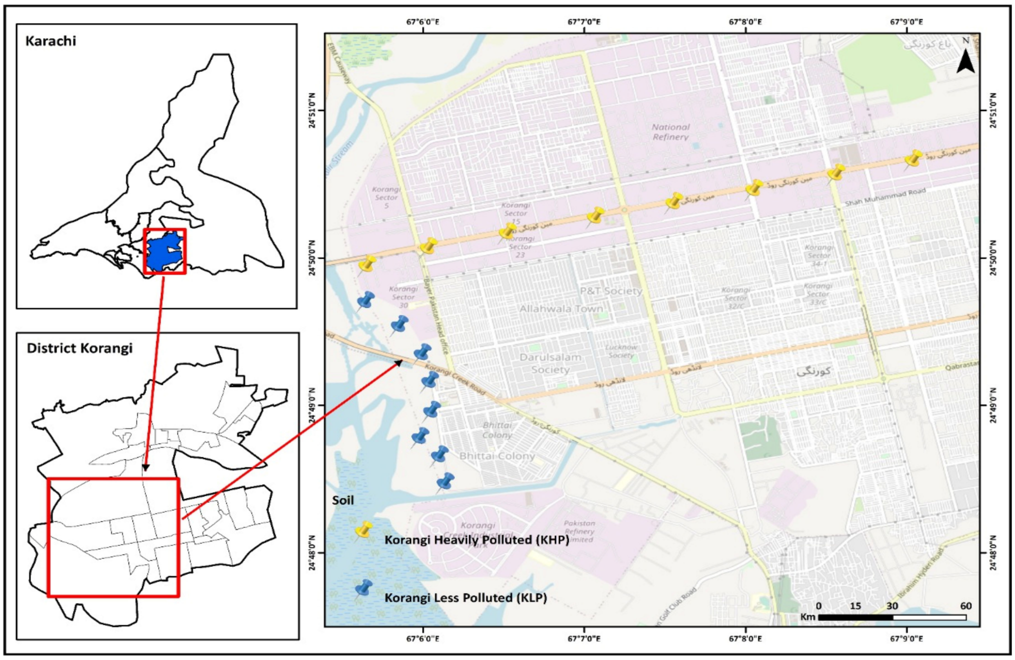

Figure 1. Map location of study area.

Table 1. Impacts of amendment on the physio-chemical characteristics of soil.

Parameters	K-HP	K-LP	FE	RP	GBC
pH (1:2 H_2O)	8.10 ± 0.2	7.95 ± 0.7	6.94 ± 0.1	7.03 ± 0.5	9.7 ± 0.01
Electrical conductivity ($dScm^{-1}$)	1.26 ± 0.9	1.84 ± 0.8	1.71 ± 0.3	0.21 ± 0.3	1.361 ± 0.9
Water holding capacity (%)	31.20 ± 0.2	34.25 ± 0.1	32.08 ± 0.4	38.14 ± 0.8	66.14 ± 0.4
Grain size distribution sand %	74.15 ± 1.0	60.21 ± 0.4	-	-	-
Silt %	8.85 ± 0.2	2.59 ± 0.4	-	-	-
Clay %	17 ± 0.3	37.2 ± 0.4	-	-	-
Soil texture	Sandy clay	Sandy loam	-	-	-
Lime $CaCO_3$ %	9.2 ± 0.1	7.8 ± 0.9	-	-	-
Organic matter (%)	0.94 ± 0.16	2.70 ± 0.10	-	-	6.33 ± 0.14
Total organic carbon (g/kg)	1.7 ± 0.26	4.7.17	-	-	10.89 ± 0.24
Soil organic carbon (g/kg)	5.5 ± 1.0	15.7 ± 0.6	-	-	36.5 ± 1.0
Cu (mg/kg)	63.6 ± 0.2	41.3 ± 0.5	0.218 ± 0.6	1.142 ± 0.3	0.29 ± 0.2
Fe (mg/kg)	300.9 ± 0.9	309.02 ± 0.1	302.1 ± 0.5	306.2 ± 0.5	9.5 ± 0.7
Ni (mg/kg)	0.62 ± 0.1	0.64 ± 1.2	0.954 ± 0.3	0.280 ± 0.4	0.035 ± 0.2
Cd (mg/kg)	0.23 ± 0.5	0.19 ± 1.5	0.09 ± 1.1	0.02 ± 1.5	0.01 ± 1.2
Pb (mg/kg)	0.47 ± 0.4	0.44 ± 0.6	1.28 ± 0.8	4.18 ± 0.5	0.064 ± 0.6
Co (mg/kg)	0.16 ± 0.7	0.15 ± 0.4	0.183 ± 0.7	0.25 ± 0.1	-
Cr (mg/kg)	6.90 ± 0.6	5.71 ± 0.5	0.948 ± 0.3	1.90 ± 0.8	0.256 ± 0.2
Zn (mg/kg)	91.6 ± 0.4	87.2 ± 0.3	1.810 ± 0.7	2.7 ± 0.2	0.168 ± 0.7
Biochar yield (g/100 g biomass)	-	-	-	-	31.25 ± 0.1

K-HP = Korangi heavily polluted, K-LP = Korangi less polluted, FE = fuller earth, RP = rock phosphate and GBC = grapefruit biochar.

2.2. Material Collection and Biochar Preparation

In the present study, three different immobilizing agents: fuller earth (FE), rock phosphate (RP), and grapefruit made biochar (GBC), were used alone and in mixed form to immobilize TMs in two polluted soils. Fuller earth was collected from the local area of Multan, Pakistan, while rock phosphate was purchased from Kakul mine in Haripur, Hazara of Khyber Pakhtunkhwa, and the grapefruit peel was collected from a local fruit and juice shop of Karachi, Pakistan. The grapefruit peels were kept in a porcelain crucible, covered with lid, and pyrolyzed under the absence of oxygen in a muffle furnace at ≤500 °C temperature and the residence time was kept at 3 h.

2.3. Experimental Design and Treatments

The present study was performed in an ambient condition aiming to assess the effectiveness of amendments on the fixation and absorption of Cu, Zn, Fe, and Cd by maize crop. The studied additives include fuller earth, (FE), rock p (RP), and grapefruit-made biochar (GBC) < 500 °C alone and combined were applied at 1% (w/w), all the entire additives were carefully ground to pass through <2 mm and carefully mixed with contaminated soils, except for untreated control soil samples. Approximately, 10.0 g of each modification was applied to a fraction of 1.0 kg of air-dried samples, which were placed in pots 20 cm in diameter and 25 cm in height.

This design includes an entirety of 42 pots (2 types of soils × 7 divisions of treatments × 3 replicates 1 plant). The treatments setup was as follows: (T1) un-amended control (CK); (T2) fuller earth 1% (FE1%); (T3) rock phosphate 1% (RP 1%); (T4) grapefruit biochar 1% (GBC 1%); (T5) fuller earth 1% + rock phosphate 1% (FE 1% + RP 1%); (T6) fuller earth 1% + grapefruit biochar 1% (FE 1% + GBC 1%); and (T7) rock phosphate 1% + grapefruit biochar 1% (RP 1% + GBC 1%). The soils and immobilizing agents were carefully mixed before being placed in the pots. All the pots were watered with roughly 300 mL of tap water to achieve a moisture content of approximately 65% of the field capacity by Hussain et al. [30]. All the pots were equilibrated for one month in order to achieve a chemical reaction. Maize seeds were also sterilized for 10–15 min in a suspension of H_2O_2 (2% v/v) before being washed three times in pure water. After 10–15 days, around 5.0 seeds were produced and trimmed to 3.0 plants in each pot. At the time of germination, the field capacity was preserved at around 80%. The lost evaporated water from each pot was maintained on a daily basis. All maize plants were harvested 45 days after they were planted.

2.4. Sample Analysis

2.4.1. Soil and Additives Analysis

All the chemical solutions were prepared using de-ionized water and all the chemicals used in our study were of pre-analytical grade. The soil EC and pH were determined using a (1:5 H_2O ratio) method [31]. Dry combustion techniques were used to measure the organic matter (OM) in polluted soils and biochar followed by the (ASTM D 2974) method. The Mastersizer 2000E laser diffractometer (Malvern, UK) was used to determine the soil texture [32]. The SOC concentration was detected by a photometric procedure at the wavelength of 590 nm using the UV– VIS spectrophotometer Cary 50 (Varian), followed by Mockeviciene et al. [33]. An automated TOC analyzer (Shimadzu TOC-V) was used to test the TOC in soils using the dry combustion method. The $CaCO_3$ was tested acid neutralization method by Jackson [34]. Approximately, 0.5 g of studied soils and amendments were digested in HCl and HNO_3- combined at a 3:1 ratio for detect the total contents of total contents of Cu, Zn, Fe, and Cd, followed by method 3050B of the US Environmental Protection Agency [35]. The amounts of Cu, Zn, Fe, and Cd in the digested soil and amendment samples were measured using the Hitachi Z-8000 Polarized Zeeman atomic absorption spectrophotometer (Pin AAcle 900T Japan).

2.4.2. Maize Plant Analysis

The maize crop was harvested 45 days after sowing. All of the plants were meticulously uprooted, washed, and then kept in paper bags for note total biomass (shoot and root) and further chemical analysis. After drying the plant dry biomass (shoots and roots) for 3–4 days at 65 °C, the weight of the dry biomass (shoots and roots) was measured. After crushing the dried shoots and roots in a small grinder, the ground plant samples were placed in plastic bags for later investigation. Approximately, 0.5 g of plant dry matter was digested in HNO_3^- and $HClO_4$ combined at a 4:1 ratio to detect the total contents of Cu, Zn, Fe, and Cd in the maize shoots and roots according to [36,37]. The total contents of Cu, Zn, Fe, and Cd in the maize plant digested samples were measured using a Hitachi Z-8000 Polarized Zeeman atomic absorption spectrophotometer (Pin AAcle 900T).

2.5. Quality Control and Statistical Analysis

The studied treatments were used in triplicate. All the reagents were used in standard protocols. Soil GBW07457 (GSS-28) and plant GBW07603 (GSV-2 maize) certified reference materials from the Chinese Academy of Geological Sciences were used for quality control. The recovery ratios of Cu, Zn, Fe, and Cd in soil ranged from 94 to 102%, 93 to 101, 96 to 104, and 92 to 103%, respectively, and those in plants ranged from 92 to 103%, 94 to 105, 91 to 103, and 95 to 104%, respectively. Statistix 8.1 software was used to statistically analyze the experimental data. Tukey's HSD test was used to compare the means of treated replications in a one-way analysis of variance at $p < 0.05$. The OriginPro 8.5 version software was also used to make the graphs. The correlation matrix analysis was performed to make correlation between maize dry biomass, soil chemical properties, Cu, Zn, Fe, and Cd in two soils and in maize shoot.

3. Results and Discussion

3.1. Impact of Additives on EC and pH

The impact of additives on EC and pH in K-HP and K-LP soils was measured after 45 days of maize crop harvesting. In K-HP soil, all the additives significantly increased the value of EC, except the alone GBC 1% amendment, where the value slightly reduced from 1.31 to 1.29 dS/cm^{-1}. However, the addition of FE1% + RP1% as a combined amendment significantly increased the EC level, ranging from 1.31 to 1.91 $dScm^{-1}$ (Figure 2a). The maximum EC in K-LP soil was observed ranging from 1.55 to 2.05 dS/cm with combined application of RP 1% + GBC1%, while the lowest EC was observed ranging from 1.55 to 1.32 dS/cm with the addition of FE 1% + RP1%, as compared with the control treatment (Figure 2b).

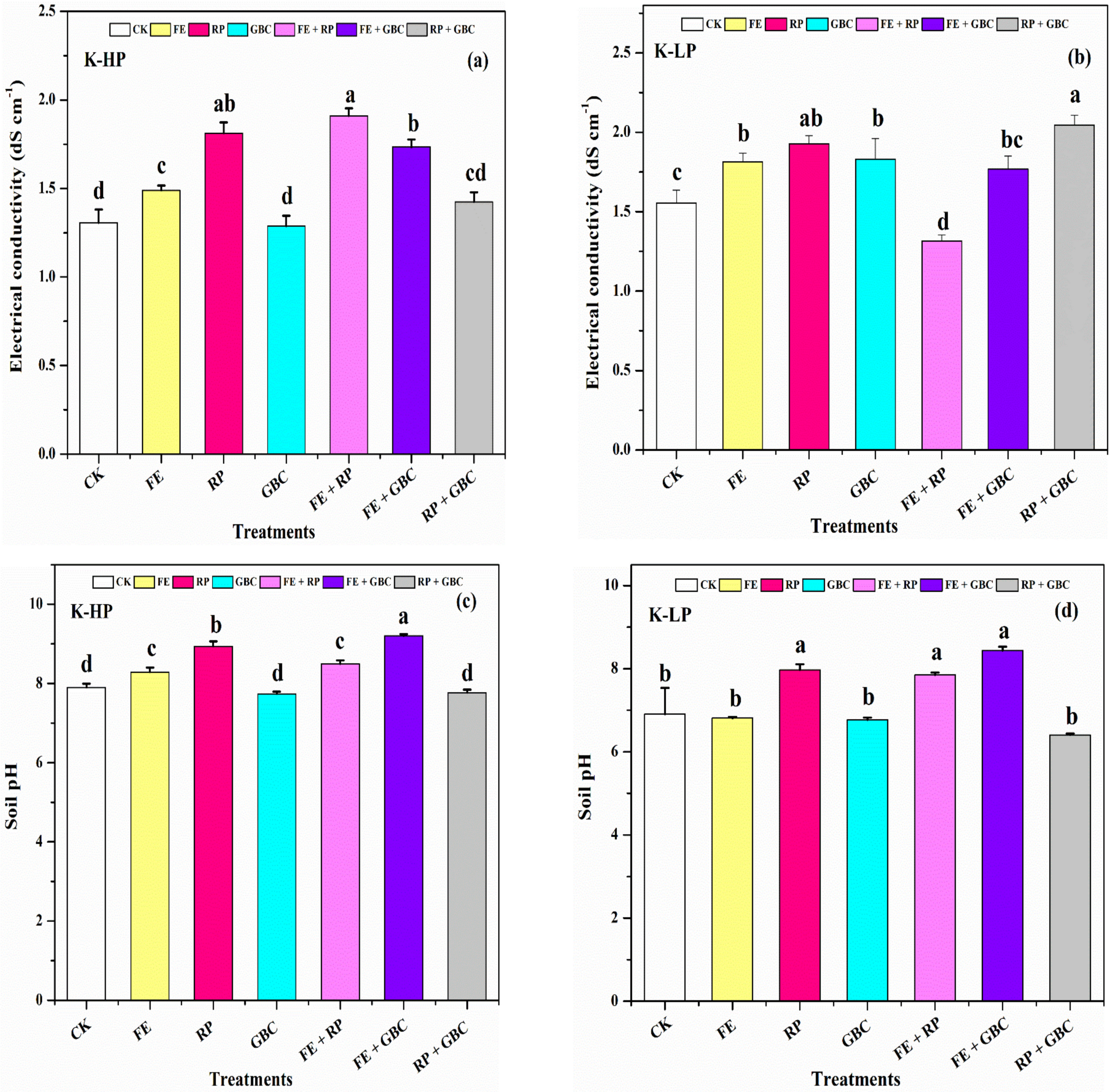

Figure 2. Influence of additives on electrical conductivity (**a**) in K-HP soil and (**b**) in K-LP soil; influence of additives on pH (**c**) in K-HP soil and (**d**) in H-LP soil. The values in a given column followed by the same letter are statistically not significantly ($p < 0.05$) using Tukey's HSD test.

Before the pot experiment, the pH value for the K-HP soil was found to be slightly basic. After 45 days of the experiment, the changes in soil pH were observed with the application of additives as compared with the control treatment. The maximum increase in soil pH was observed from control treatment 7.9 to 9.20 with the application of combined FE1% + GBC1% treatment. However, the GBC1% alone and RP1% + GBC1% combined treatments nonsignificantly reduced the pH level from 7.9 to 7.74 and 7.9 to 7.77 as compared with the control treatment (CK) (Figure 2c). The original soil pH of K-LP soil was 7.95 slightly alkaline in nature. After 45 days of the experiment, the pH of K-LP soil was significantly reduced from 6.90 to 6.81 with alone FE1%, 6.90 to 6.77 with alone GBC 1%, and 6.90 to 6.40 with combined RP1% + GBC1%. It was assumed that the alone FE1%, GBC1% and RP1% + GBC1% had a positive response on slightly reduced soil pH in the soil system after harvesting of the maize plant. Furthermore, the maximum soil pH was increased from 6.90 to 8.43 with application of combined FE1% + GBC1% as compared with the control treatment (Figure 2d). In addition, Boostani et al. [38] revealed that the soil pH was increased significantly with the addition of natural zeolite and biochar. Alaboudi et al. [39] stated that the soil pH was dramatically increased in artificial contaminated loamy sand soil with application of BC.

3.2. Impact of Additives on TOC and SOC

As compared with control treatment, the changes in total organic carbon (TOC) and soil organic carbon (SOC) were observed in K-HP and K-LP soils with the incorporation of amendments. However, the maximum concentration of TOC in K-HP soil was observed by 23.80% with the application of GBC1%, whereas the addition of RP1% reduced it by 24.61% as compared with control treatment (Figure 3a). The greatest increase in TOC concentration in K-LP was 60.50% treated with combined FE1% + GBC1%, whereas individual RP1% application and RP1% +FE1% reduced it from 11.71% to 8.78% as compared with the control (Figure 3b). In K-HP, the concentration of SOC was significantly increased by 22.52% with the application of GBC 1%, whereas the reduction in SOC was observed by 6.36% with alone FE1%, 19.57% with alone RP1%, and 7.92% with combined FE1% + RP 1% as amendments than the control treatment (Figure 3c). The concentration of SOC in K-LP was increased by 60% with the application of FE1% + GBC1% (T6). However, the reduction in SOC in K-LP soil was received by 31.17% with RP1%, and 6.34% with RP1% + GBC 1%, respectively, as compared with the control treatment (Figure 3d). Gao et al. [40] stated that the TOC in soil was increased with the rice straw biochar application. Mockeviciene et al. [33] stated that the addition of organic fertilizers exerted a significant positive effect on SOC accumulation by 0.1–0.4% more carbon as compared with the control treatment.

3.3. Impact of Additives on Organic Matter and Maize Dry Biomass

Application of the additives into the pots resulted in the significantly increased organic matter and dry biomass in both polluted soils. The maximum concentration of soil organic matter (OM) in K-HP soil was increased substantially from 1.45 to 1.94% treated with GBC1%, whereas RP1% possibly reduced it from 1.45 to 1.16% compared with the un-amended control soil sample CK (Figure 4a). In K-LP, the concentration of soil organic matter (OM) increased dramatically from 1.2 to 1.34% treated with FE1% + GBC1%, whereas alone RP1% and combined RP1% + FE 1% reduced it from 1.20 to 1.09%, and 1.20 to 1.08%, respectively, as compared with the control (Figure 4b). Alaboudia et al. [39] reported that the BC significantly increased the soil organic matter (SOM) and maize biomass at 5 and 10% dosage in artificial Pb, Cd, and Cr contaminated soil. As compared to the control, the dry biomass of the maize crop in K-HP soil was significantly increased by 14.13% with the addition of FE1% + GBC1%, but alone GBC1% and combined RP1% + GBC 1% treatments showed negative impact on maize dry and slightly reduced it by 2.02% and 1.65%, respectively, as compared with the control treatment. It was observed that the FE1% + GBC1% shows a positive impact on maize biomass, and GBC1% and RP1% + GBC1% treatments indicated a negative impact on maize dry biomass, which might be due to an increase in TOC and SOC proportion (Figure 4c). In contrast to the control, the dry biomass of soil K-LP soil significantly increased by 18.24% with the application of FE1% + GBC1%, but the application of FE1%, GBC1%, and RP1% + GBC1% treatments dramatically reduced the maize dry biomass up to 1.30%, 1.88%, and 7.25%, respectively (Figure 4d). Rehman et al. [41] revealed that the plant biomass and grain yield of both rice and wheat corps were significantly increased with the application of organic and inorganic additives.

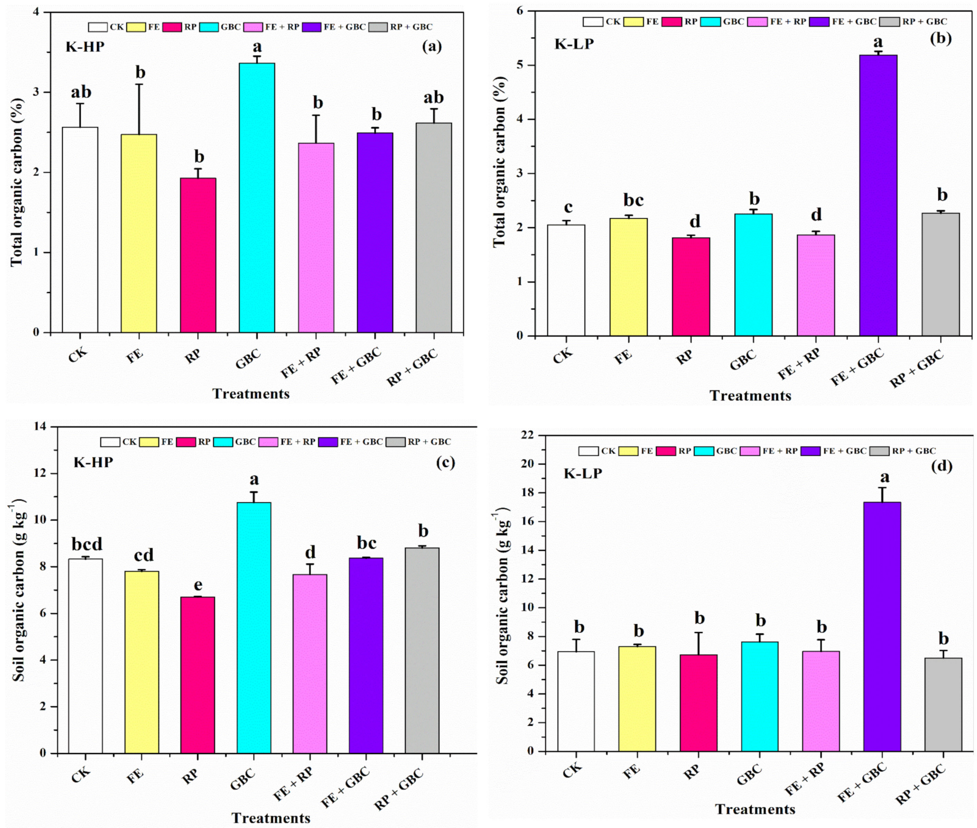

Figure 3. Influence of additives on total organic carbon (**a**) in K-HP, (**b**) H-LP; soil organic carbon, (**c**) in K-HP soil, and (**d**) in H-LP soil. The values in a given column followed by the same letter are statistically not significantly (p < 0.05) using Tukey's HSD test.

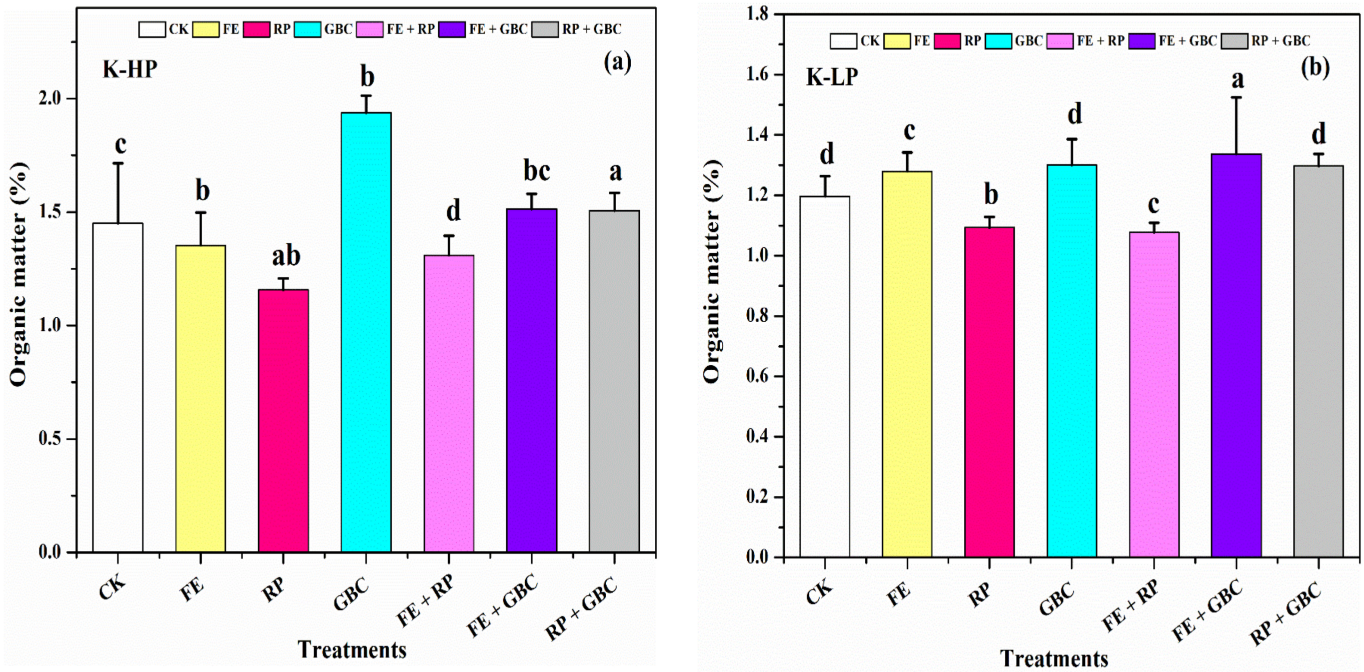

Figure 4. *Cont.*

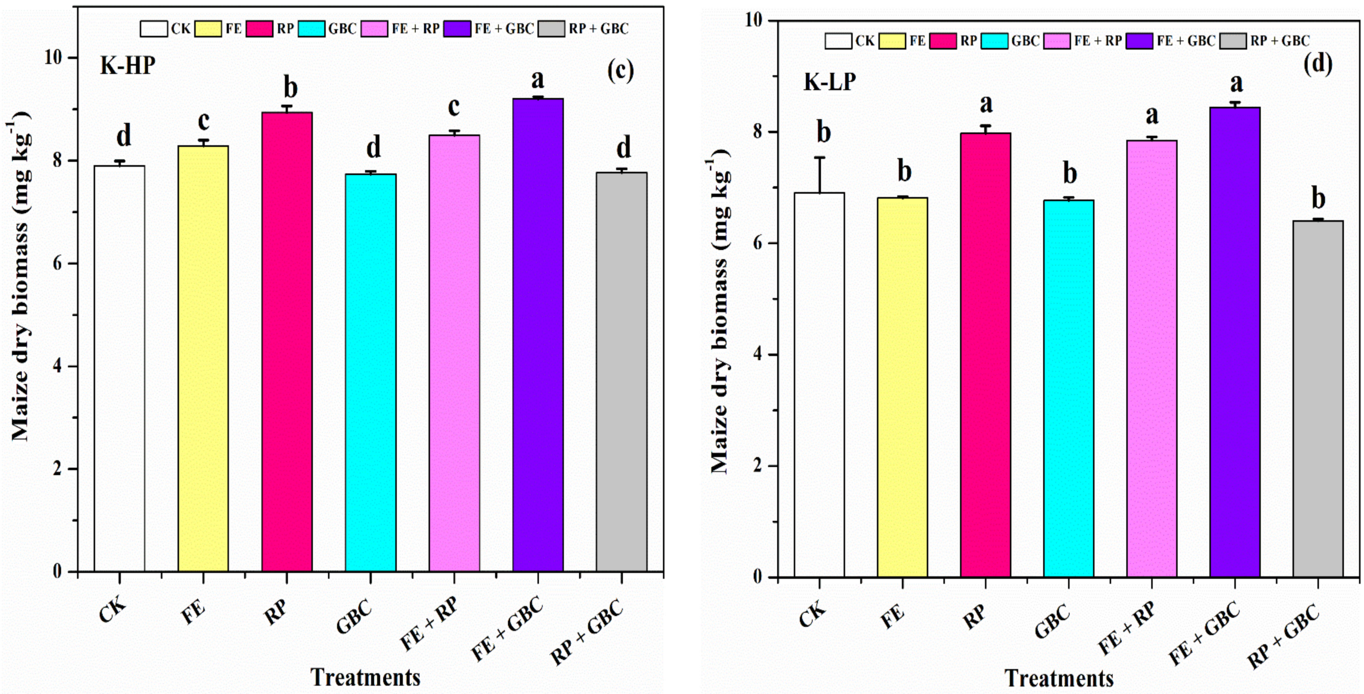

Figure 4. Influence of additives on organic matter (**a**) in K-HP soil, (**b**) H-LP soil; dry biomass (**c**) in K-HP soil, and (**d**) in H-LP soil. The values in a given column followed by the same letter are statistically not significantly ($p < 0.05$) using Tukey's HSD test.

3.4. Impact of Additives on Cu and Zn in Polluted Soils

The concentration of Cu, Zn, Fe, and Cd in K-HP and K-LP soils was tested after 45 days of maize planting. The amendments had significantly immobilized the studied Cu, Zn, Fe, and Cd in both contaminated soils. The maximum immobilization of Cu in K-HP soil was observed by 36% with the application of mono GBC1% treatment, however the maximum mobilization of Cu in K-HP soil was observed by 99.03% with the alone application of FE1%, as compared to the control (Figure 5a). The Cu concentration in K-LP soil was reduced largely up to 90.24% with compound (FE1% + GBC1%), but the maximum mobilization of Cu in K-LP soil was observed by 90.96% with the combined (FE1% + RP1%), as compared to control (Figure 5b).

The immobilization of Zn in K-HP and K-LP soil was observed with the application of additives, while, the highest stabilization of Zn in K-HP was received by 11.90% with application alone of FE1%, but the application of combined FE1% + GBC1% as treatments mobilized the Zn 99.7% as compared with the control (Figure 5c). Furthermore, in the case of K-LP soil, the maximum immobilization of Zn in K-LP soil was received by 28.6% with FE1% and RP1% + GBC1%, respectively, nonetheless the maximum mobilization of Zn in K-LP soil was 61.11% with GBC1%, as compared with other treatments (Figure 5d). Palansooriya et al. [42] revealed that the combined application of additives had great potential to stabilize TMs in soil–plant.

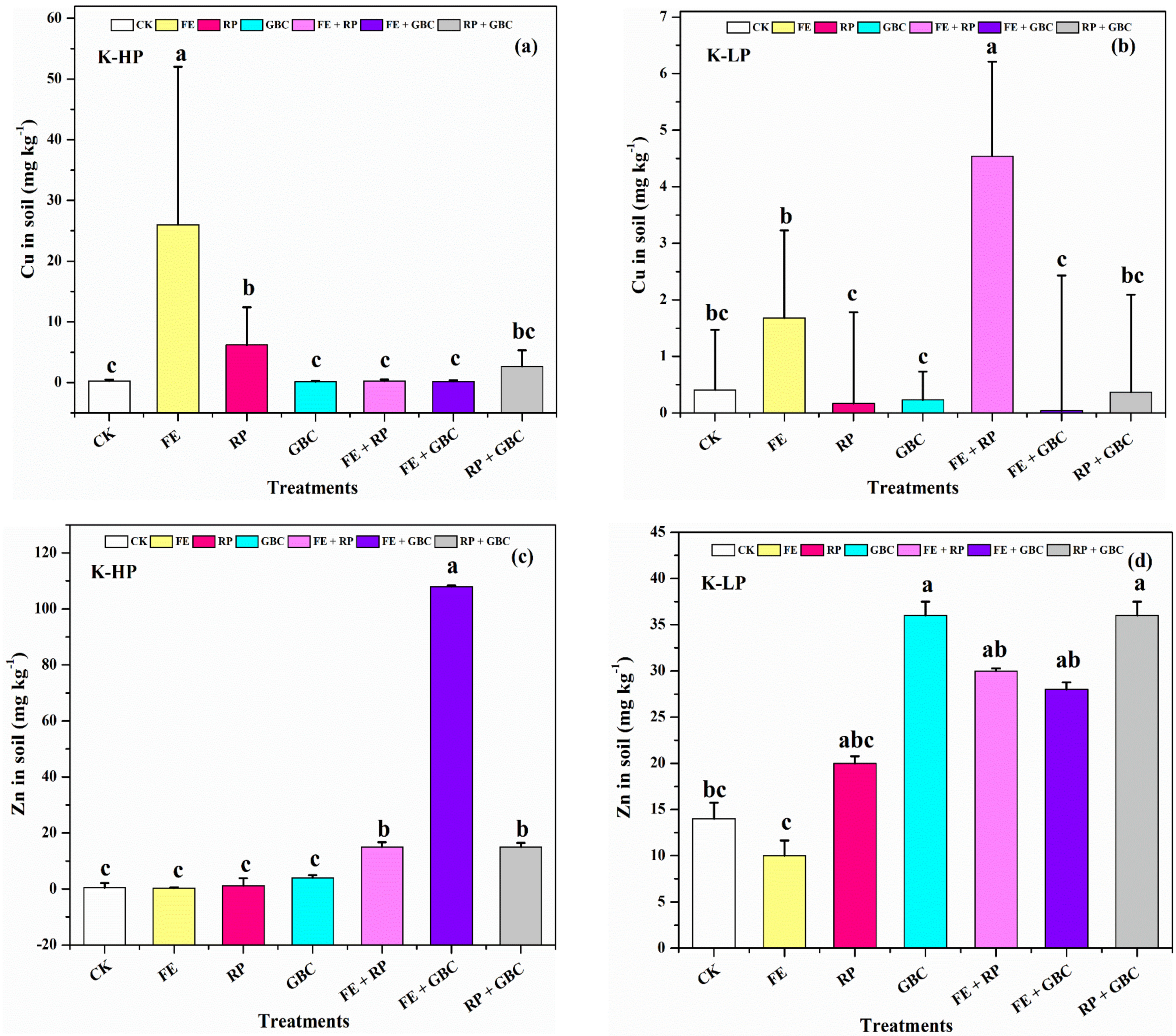

Figure 5. Influence of additives on Cu in (**a**) in K-HP soil and (**b**) H-LP soil; influence of additives on Zn, (**c**) in K-HP soil, and (**d**) in H-LP soil. The values in a given column followed by the same letter are statistically not significantly ($p < 0.05$) using Tukey's HSD test.

3.5. Impact of Additives on Fe and Cd in Polluted Soils

The highest immobilization rate of Fe in K-HP soil was 98.97% with the application of combined RP1% + GBC1% amendments, whereas the application of FE1% mono treatment enhanced the Fe concentration up to 43.10% as compared with the control treatment (Figure 6a). The application of RP1% + GBC1% in K-LP soil dramatically immobilized the Fe concentration up to 22.22%, however the maximum mobilization of Fe in K-LP soil was observed by 17% with the application of alone RP1% treatment (Figure 6b). The maximum reduction in Cd in K-HP soil was observed by 51.9% with the combined FE1% + GBC1% treatment, whereas the mobilization of Cd in K-HP soil was received by 1.57% with alone GBC1% treatment (Figure 6c). As compared with the control treatment, the highest stabilization of Cd in K-LP soil was 57.05% with FE 1% + GBC 1% over than other treatments (Figure 6d). Alaboudi et al. [38] stated that the green waste made BC significantly reduce the Cd in contaminated soil by 85%. It was observed that the synergistic interactions between the materials and their influence on immobilization and accumulation of TMs were observed with application of alone and mixed additives. Munir et al. [43] conducted a study on the synergistic impacts of BC and processed fly ash on bioavailability, transformation, and accumulation of TMs by maize in coal mining-polluted soil and found that the alone application of BC and processed fly ash significantly enhanced Fe bioavailability and combined BC, and processed fly ash application reduced Fe bioavailability in polluted soil.

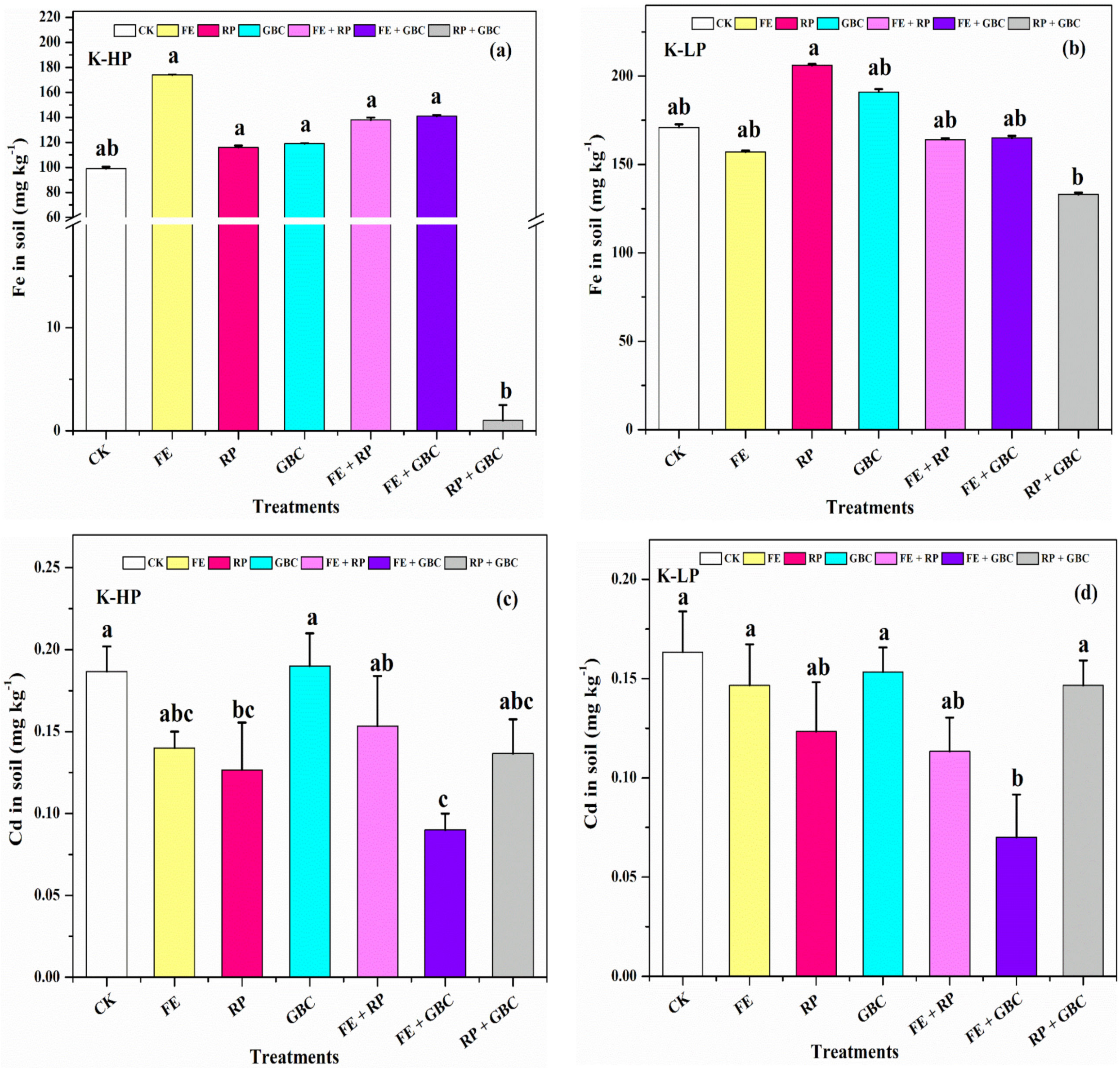

Figure 6. Influence of additives on Fe in (**a**) in K-HP soil and (**b**) H-LP soil; influence of additives on Cd, (**c**) K-HP soil, and (**d**) in H-LP soil. The values in a given column followed by the same letter are statistically not significantly ($p < 0.05$) using Tukey's HSD test.

3.6. Impact of Additives on Uptake of Cu and Zn into Maize Shoot

The greatest Cu content in maize shoot was evidently reduced by 13.04% with application of combined FE1% + GBC1% treatment, nonetheless, the uptake of Cu in maize shoot was detected by 36.11% with application of alone RP 1% as compared with the control (Figure 7a). It was observed that the application of alone and combined additives in K-LP soil potentially reduced the update of Cu by maize shoot, while the greatest reduction in Cu uptake in the shoot by maize plant was 71.77% with the application of FE1% treatment, as compared with the control (Figure 7b). In terms of Zn in K-HP soil, the application of alone and combined amendments had non-significantly enhanced the uptake of Zn by maize shoot. However, the maximum uptake of Zn by maize shoot was observed by 99.57% with application of alone GBC1% treatment. It might be due to the alone application of organic amendment, which may favor to release organic acids from increasing the organic matter content as compared with un-amended soil. It was observed that the application of GBC1% can be successfully used to enhance Zn phytoremediation, because 70% rice cultivated soils of Pakistan are already deficient in Zn (Figure 7c). In case of K-LP soil, the maximum reduction in Zn in the shoot by maize plant was 75% with addition of FE1%, but the maximum uptake of Zn by maize shoot was received by 50% with RP1% + GBC1% as compared with other treatments (Figure 7d). According to Nzihou and Sharrock [44], phosphate can be used to develop environmentally friendly processes for cleaning TMs in contaminated soil and reduce their accumulation by plants.

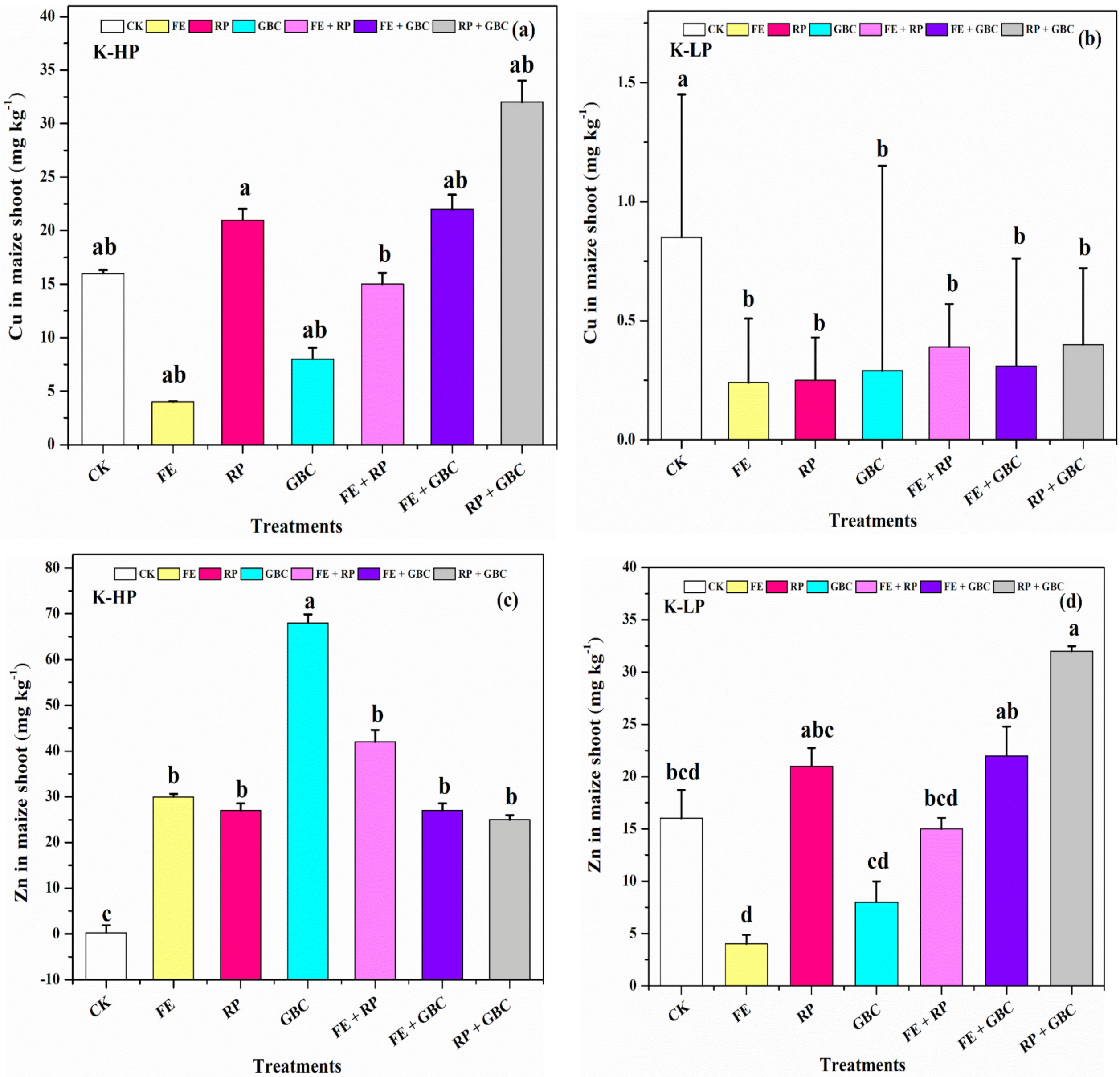

Figure 7. Influence of additives on Cu in (**a**) K-HP maize shoot and (**b**) K-LP maize shoot; influence of additives on Zn in (**c**) K-HP maize shoot and (**d**) in H-LP maize shoot. The values in a given column followed by the same letter are statistically not significantly ($p < 0.05$) using Tukey's HSD test.

3.7. Impact of Additives on Uptake of Fe and Cd by Maize Shoot

When comparing the impact of additives on K-HP soil with control treatment (Figure 8a), the Fe concentration in the shoot by maize was evidently reduced to 32.14% with the application of FE1% + RP1%, whereas the observed uptake of Fe in the shoot of maize plant was observed at 63.16% with the combined application of FE1% + GBC1%. The absorption of Fe in the shoot tissue was considerably reduced by 28.6% with FE1% application, but the maximum uptake of Fe (28.9%) in the shoot of maize plant was detected with FE1% + GBC1% in K-LP soil (Figure 8b). The absorption of Cd in the shoot of maize plant was considerable reduced in a greater extent up to 74% with the combined application of FE1% + RP1%, however, GBC1% treatment showed 16.7% enhanced uptake in Cd in the shoot of a maize plant of K-HP soil (Figure 8c). The higher reduction in Cd (90%) content in the shoot of maize plant was detected in K-LP soil with combined application of FE1% + RP1% (Figure 8d). It is considered a viable remediation option to reduce TM bioavailability by plants. Rizwan et al. [45] stated that stress caused by TMs possesses the opposite impact of seed germination, nutrient statues, photosynthesis process, growth, and development. It could be due to variance in plant type, soil type, amendment dose, size, TM type, forms, and exposure duration. Baghour et al. [46] stated that the root zone temperature influenced the phytoextraction of iron in polluted soil. Rizwan et al. [47] revealed that the harmfulness response of maize to Cd differs with plant genotypes, growth, and stress period; furthermore, the exogenous application of organic and inorganic amendments was used for enhancing the Cd tolerance of maize. Ran et al. [48] found that the uptake of Cd by brown rice reduces significantly with the application of combined amendments. Munir et al. [43] revealed the uptake of Fe by maize plant significantly reduced with application of BC and also BC process fly ash in coal mining polluted soil.

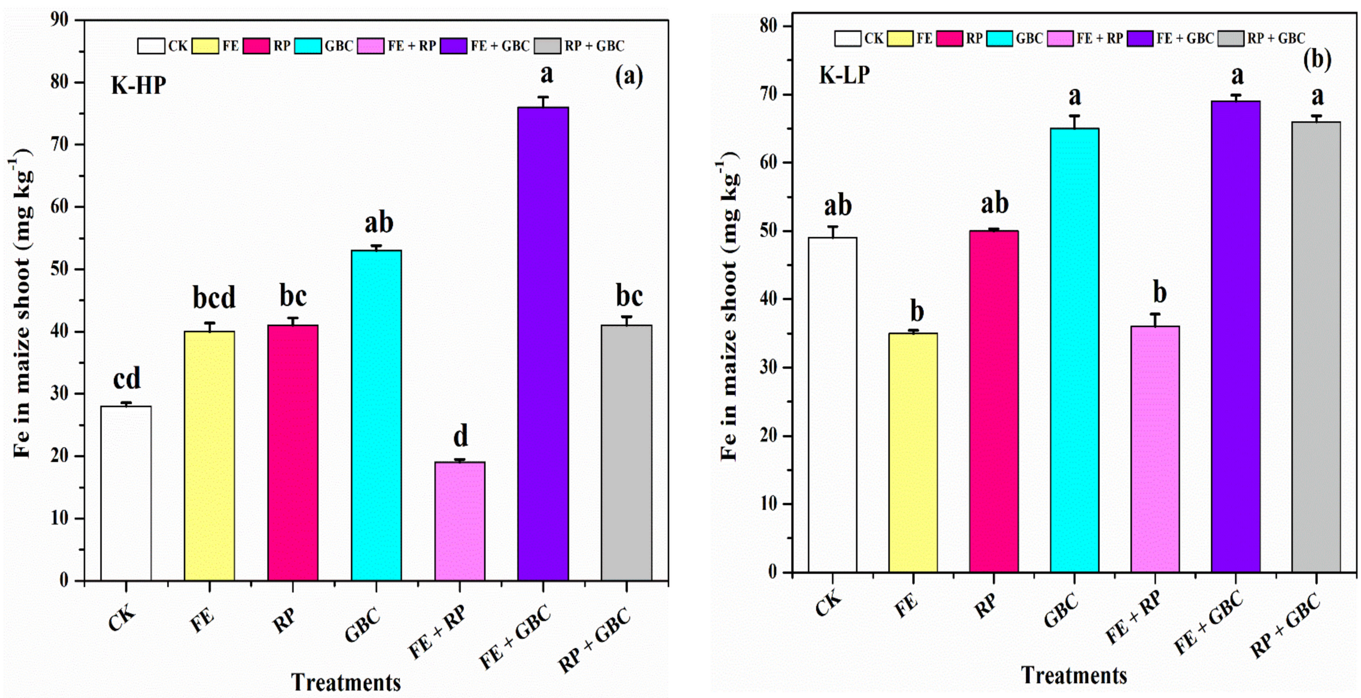

Figure 8. *Cont.*

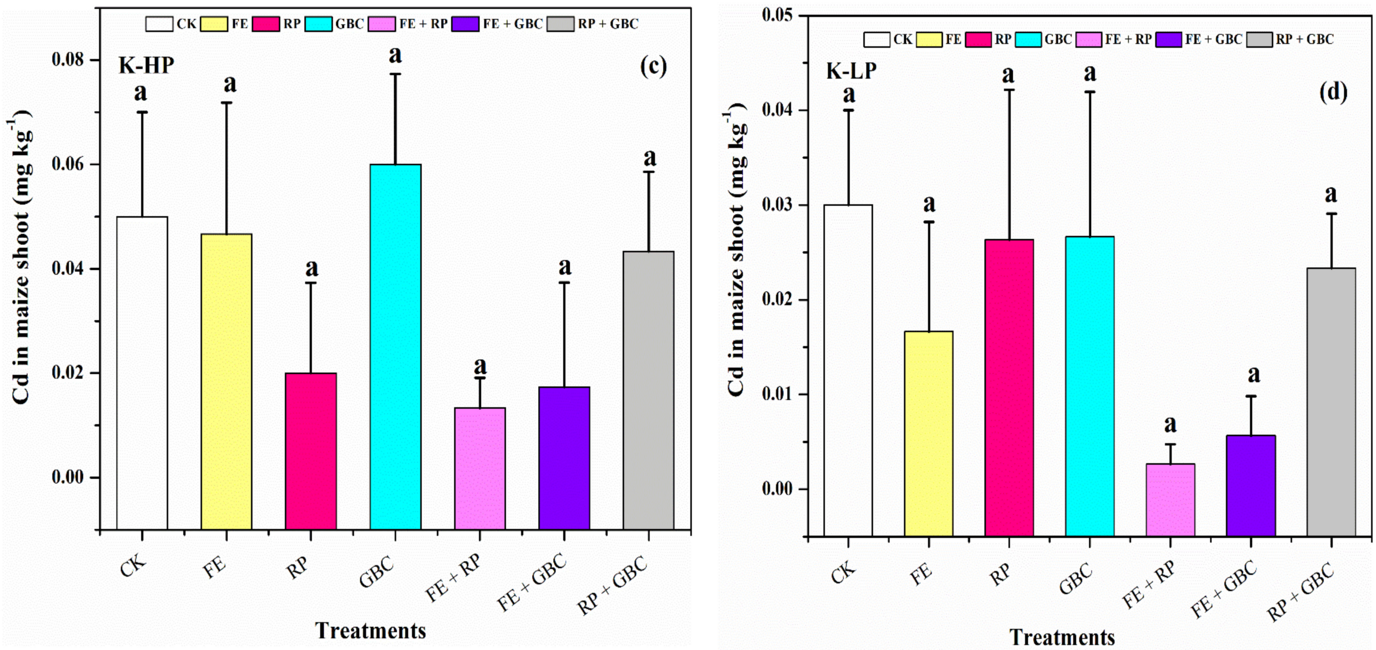

Figure 8. Influence of additives on Fe in (**a**) in K-HP maize shoot and (**b**) H-LP maize shoot; influence of additives on Cd in (**c**) K-HP maize shoot and (**d**) in H-LP maize shoot. The values in a given column followed by the same letter are statistically not significantly ($p < 0.05$) using Tukey's HSD test.

3.8. Correlation Matrix between Studied Parameters

The correlation matrix analysis was performed to investigate the relationship between, EC, pH, TOC, SOC, OM, dry biomass, Cu, Zn, Fe, and Cd in K-HP soil and K-LP soils and uptake of Cu, Zn, Fe, and Cd in the shoot of the maize plant was investigated (Figure 9a,b). As shown in K-HP soil, Cd uptake in maize shoot, TOC, OM, and SOC were positively correlated with Cd in soil, but EC, dry biomass, pH, Zn in soil, and Fe in maize shoot was negatively correlated with Cd in soil. The TOC, OM, and SOC were found to be significantly correlated with Cd in maize shoot, whereas the EC, dry biomass, pH, and Zn in soil were negatively correlated with Cd in maize shoot. The OM, SOC, and Zn in maize shoot were significantly correlated with TOC and EC, dry biomass and pH were negatively correlated with TOC. The SOC and Zn in maize shoot had a positive significant correlation with OM and a negative correlation was observed with EC, dry biomass, and pH. The Zn in maize shoot has a positive association with SOC and EC, dry biomass, and pH. The dry biomass and pH were positively correlated with EC. The soil pH, Zn, and Fe in maize shoot were found to be positively correlated maize dry biomass. The Zn in soil and Fe in maize shoot were positively associated with pH, and Fe in maize shoot was positively correlated with Fe in maize shoot grown in K-HP soil (Figure 9a). In the case of K-LP soil, the Zn, Fe, and Cd in maize shoot were positively correlated with EC, but Cu in soil was negatively correlated, and the relation was significant. The Zn in soil and Fe in maize shoot were positively correlated with Zn in maize shoot. Furthermore, Fe, in maize shoot was positively correlated with Zn in soil. Indeed, SOC, OM, and TOC have positive significant correlation with Fe in maize shoot, but negative correlation with Cu in soil was observed with EC in soil and Fe in maize shoot. The pH, SOC, OM, and TOC were found to be significant correlated with maize dry biomass, but Cd in soil was negatively correlated with maize dry biomass. Furthermore, SOC, OM, and TOC were positively correlated with soil pH, whereas the negative correlation of Cd in soil was observed with pH. However, OM and TOC were positively correlated with SOC and negatively associated with Cd in soil. The TOC was positively correlated with OM and negatively associated with Cd in soil. In addition, the Cd in soil was negatively correlated with TOC, likewise, the Cd in maize shoot was negatively associated with Cu in soil. The positive correlation of Cd in maize shoot was observed with Cd in soil (Figure 9b). Pinto-Poblete et al. [49] stated that Cd content was negatively correlated with strawberry biomass; the higher the level of biomass, the inferior the Cd concentration. Furthermore, Cd content was adversely associated with the rest of the parameters.

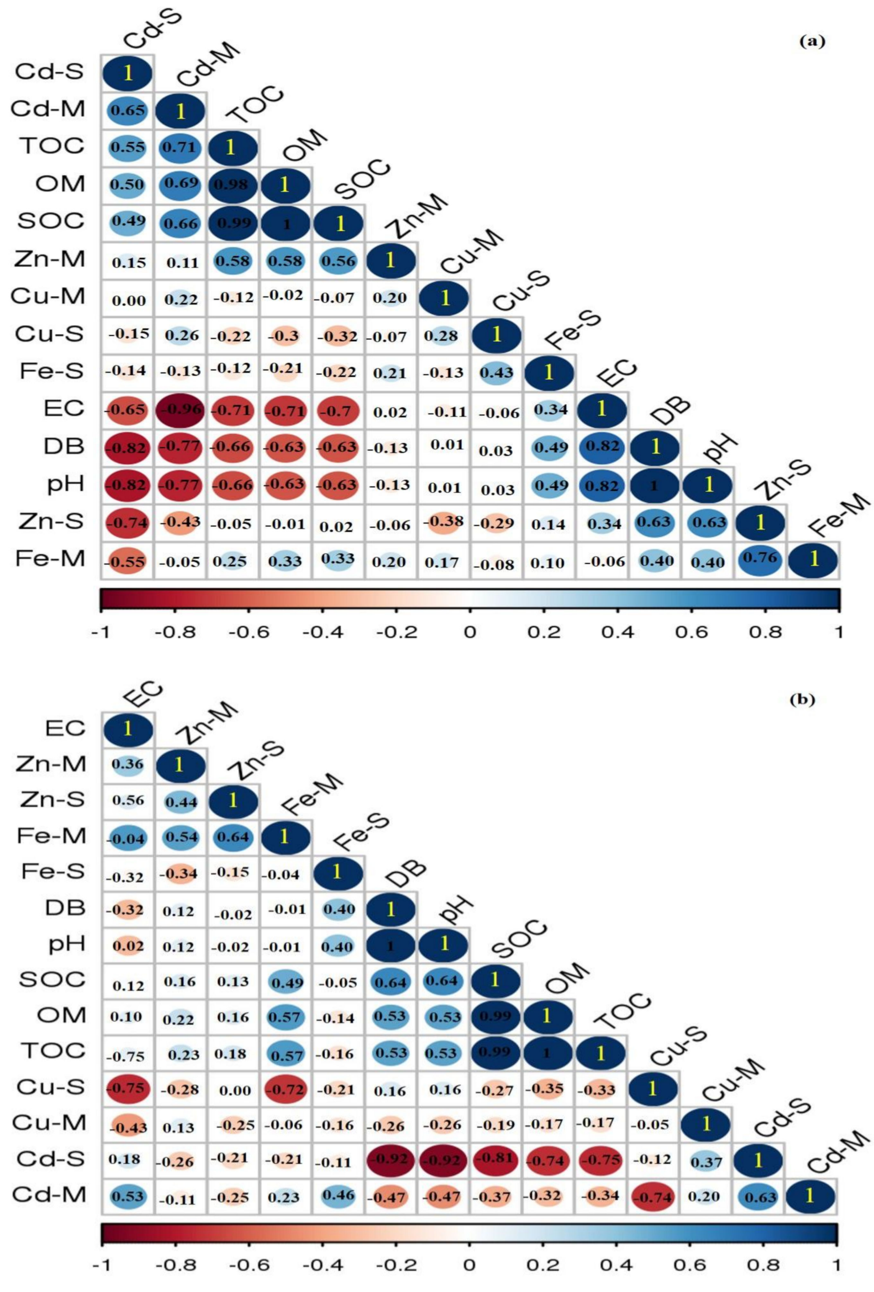

Figure 9. Correlation matrix between studied parameters in K-HP (**a**) and K-LP soils (**b**).

4. Conclusions

In the present work, alone and combined impacts of fuller earth, rock phosphate, and grapefruit peel-made biochar on the phytomanagement of Cu, Zn, Fe, and Cd in K-HP and K-LP soils and accumulation by maize plant were investigated. The dry biomass of maize plant was observed to a greater extent by FE 1% + GBC 1% in K-HP and K-LP soils. The higher stabilization of Cu was observed with the application of GBC 1%, whereas alone FE 1% treatment enhanced the Cu content in K-HP soil. The Zn concentration in K-HP soil was reduced with the treatment of RP 1%, whereas FE 1% + GBC 1% enhanced the solubility due to changes in soil pH, OM, TOC, and SOC. Likewise, the use of FE1% and RP 1% + GBC 1% significantly reduced Zn in K-LP soil. The maximum stabilization of Fe was observed with RP 1% + GBC 1%, whereas an increase in Fe content was observed with FE1% in K-HP and RP 1% in K-LP soil. The immobilization of Cd was observed with the employment of FE 1% + GBC 1% in K-HP and K-LP soils, but GBC 1% alone enhanced the solubility in K-HP soil. The application of FE 1% + RP 1% and FE1% treatments reduced the uptake of Cu maize shoot, however the results are controversial for alone RP 1% treatment. The uptake of Zn by maize shoot was reduced with FE1%, unlike the influences of GBC 1% and RP 1% + GBC 1% treatments. The application of FE 1% + RP 1% and FE1% treatments evidently reduced Fe uptake by maize shoot, dissimilar to the findings observed by the FE 1% + GBC 1% treatment. The Cd uptake by maize shoot was reduced with FE 1% + RP 1% rather than alone GBC 1% treatment. Overall, alone and combined effects of fuller earth, rock phosphate, and biochar (grapefruit peel) have potential to stabilize toxic metals in contaminated soils. Hence, it is suggested that long-term field experiments are needed to verify the stability of proposed substances for safe crop production and ameliorate the TM leachate, enzymatic activity, macro/micro-nutrient sand/or salinity in polluted soils.

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