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Diminishing Heavy Metal Hazards of Contaminated Soil via Biochar Supplementation

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Abstract: Depending on the geochemical forms, heavy metal (HM) accumulation is one of the most serious environmental problems in the world and poses negative impacts on soil, plants, animals, and humans. Although the use of biochar to remediate contaminated soils is well known, the huge quantities of waste used and its recycling technique to sustain soil in addition to its use conditions are determinant factors for its characteristics and uses. A pot experiment was conducted in a completely randomized block design to evaluate metal forms and their availability under the application of garden waste biochar (GB) pyrolyzed at different temperatures, and a sequential extraction procedure was designed to fractionate Pb, Cd, Zn, and Cu of the contaminated soil. The results show that the TCLP-extractable Pb, Cd, Zn, and Cu were significantly decreased depending on the biochar addition rate, pyrolysis temperature, and tested metal. The acid extractable fraction was significantly decreased by 51.54, 26.42, 16.01, and 74.13% for Pb, Cd, Zn, and Cu, respectively, at the highest application level of GB_{400} compared to untreated pots. On the other hand, the organic matter bound fraction increased by 76.10, 54.69, 23.72, and 43.87% for the corresponding metals. The Fe/Mn oxide bound fraction was the predominant portion of lead (57.25–62.84%), whereas the acid fraction was major in the case of Cd (58.06–77.05%). The availability of these metals varied according to the application rate, pyrolysis temperature, and examined metals. Therefore, the GB is a nominee as a promising practice to reduce HM risks, especially pyrolyzed at 400 °C by converting the available fraction into unavailable ones.

Keywords: heavy metals; garden biochar; pyrolysis; speciation; availability

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Citation: Awad, M.; El-Sayed, M.M.; Li, X.; Liu, Z.; Mustafa, S.K.; Ditta, A.; Hessini, K. Diminishing Heavy Metal Hazards of Contaminated Soil via Biochar Supplementation. *Sustainability* **2021**, *13*, 12742. https://doi.org/10.3390/su132212742

Academic Editor: Zakaria Solaiman

Received: 13 October 2021
Accepted: 13 November 2021
Published: 18 November 2021

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1. Introduction

Contamination of soils with heavy metals (HMs) has been considered one of the most serious worldwide problems that threatens the ecosystem and human life [1–3]. The Industrial Revolution, extensive mining, smelting, effluents discharge, and intensive agricultural fertilization threaten soil quality, food safety, and human health [4,5]. In China, Shaoguan city, located in northern Guangdong Province, contained acid soils contaminated with HMs due to the discharge of industrial effluents for more than 50 years and mining

activities [6]. These soils have low pH values that cause high mobility of some HMs, especially Cd and Pb.

Over the past few decades, many methods have been used as a new tool to overcome the seriousness of the pollutants in contaminated soil, including stabilizing, drilling, dumping, soil washing, and electro carbons [7,8]. The use of organic or inorganic materials for stabilizing HMs is considered a faster, more effective, and environmentally friendly management technique that reduces their mobility and bioavailability by transforming them into unavailable forms in agricultural soils [1,4,9–11]. Among organic amendments, biochar is a carbon-rich amendment produced through the pyrolysis of the biomass [12]. Several factors (feedstock particle size and type, as well as pyrolysis temperature) affect biochar characteristics and functions. The wide range of biochar properties enables it to be the most suitable material for dealing with and remediating various HM-contaminated soils [13]. The key properties of biochar are affected by pre-treatments resulting in enhancing biochar's ability to immobilize HMs [14].

In general, HMs' toxicity and their movement in the soil depend not only on their concentration but also on their chemical forms and the environmental conditions [15,16]. The total metal concentration might not provide the basic information about the biological availability of potentially toxic metals. However, identification of the geochemical forms provides some facts about their movement and availability as well as their toxicity [11,17–19]. Therefore, understanding the chemistry of HMs is necessary to know their bioavailability, chemical form, types, and solid phase, which greatly affect their fate and redistribution [20–22]. These forms may be regulated by ion exchange, water complexity, stabilization, and plant uptake [11,23].

Sequential extraction and fractionation procedures might obtain more information on the origin, bioavailability, and toxicity of HMs. It is the most widely accepted and used method to assess the redistribution, bioavailability, and toxicity of metals in different chemical forms [21,24]. It starts with the use of the weakest extract and ends with the use of the most strong and aggressive extractants, followed by the decreasing order of solubility, divided into three to seven fractions [25]. The redistribution of metals in multi-metal contaminated soils modified by garden waste at low and high pyrolysis temperature is still unclear. We hypothesized that recycling a huge quantity of garden wastes as garden biochar (GB) at different pyrolysis temperatures may have a beneficial effect on soil properties and metal remediation via a decrease in the available metal fraction (the acid-soluble metals) at the expense of the unavailable form (the organic matter and oxide pounds). The main objectives of the current study were to assess the effects of biochar pyrolyzed at different temperatures and its application rates on soil properties, as well as the transformations of lead, cadmium, zinc, and copper in contaminated soils. We also wanted to find the optimum application rate and pyrolysis temperature that mitigate the environmental hazardous effects of HMs under acidic soil conditions.

2. Materials and Methods

2.1. Soil Samples

Multi-contaminated topsoil (0–20 cm) samples were collected from different locations of Shaoquan city, Guangdong Province, China, to assess Pb, Cd, Zn, and Cu transformation and their bioavailability as affected by garden waste biochar (GB) application at different pyrolysis temperatures. The collected soil samples were air-dried and passed through a 5 mm sieve after grinding with a stainless-steel grinder to be ready for a pot experiment. A composite soil sample was taken, then sieved through a 2 mm sieve and kept for soil chemical analysis. Particle size distribution was determined as described by [26]. The soil acidity was measured by pH meter of water/soil suspension at a 1:2.5 ratio and the electrical conductivity (EC) was also estimated in a 1:10 ratio (soil:water ratio, w/v) using an EC meter [26]. Total soil metal contents were extracted using the digested eluent of the soil samples with concentrated acids of HF, HNO_3, and HCl [26]. After digestion, different fractions of eluent were run on an atomic absorption spectrometer (AA 800, Perkin Elmer

Co., 14775 E Hinsdale Ave, Centennial, CO, USA) for different HM determinations. Organic matter was estimated by wet oxidation according to [27].

2.2. Biochar Preparation

Garden wastes (paper, grass, and small stems) were collected by the well-known Dadi Yuan Line Company in Sounded city, China, which air-dried the wastes and then oven dried them for 2 h at 105 °C and bundled them in a sizable package. Some packages were subjected to prepare it as garden waste biochar (GB) manually in the laboratory, which was pyrolyzed at a temperature of 400 °C or 600 °C for 3 h (it remained in the muffle furnace, which was under limited oxygen conditions, for 3 h after the temperature reached 400 °C or 600 °C) and denoted as GB_{400} and GB_{600}, respectively. The prepared biochar was crushed by a stainless-steel mill and sieved through a 0.1 mm sieve. Some selected characteristics of both the tested soil and the biochar were measured according to [28] and are shown in Table 1.

Table 1. Some physicochemical properties of the studied soil and the utilized biochars.

Property	Unit	Soil	Garden Waste Biochars (GB)	
			GB_{400}	GB_{600}
Clay	g kg^{-1}	258	-	-
Silt	g kg^{-1}	319	-	-
Sand	g kg^{-1}	423	-	-
Texture		Loam	-	-
Organic matter	g kg^{-1}	23.45	867	862
EC (1:5)	dS m^{-1}	0.92	5.50	7.00
pH (1:2.5)	-	5.54	11.00	11.50
Total Cd	mg kg^{-1}	2.44	ND	ND
Total Pb	mg kg^{-1}	980	7.00	11.25
Total Zn	mg kg^{-1}	1019	82.00	107.00
Total Cu	mg kg^{-1}	34	18.50	26.90

ND; not detected. Each value represents the mean of three replicates.

2.3. Pot Experiment

Plastic pots were filled with 1.5 kg of the tested soil samples that were previously mixed well with different garden biochars at rates of 0% (CK), 2%, 4%, and 6% (*w*/*w*) in three replicates. In a greenhouse pre-set for 18–25 °C and 60–70% relative humidity, each pot was kept moist with tap water (70% of the field capacity) for the duration of the experiment (two months). Chemical analysis of the biochar granules was carried out using scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX) analysis. The functional groups involved in adsorption were determined by Fourier-transform infrared (FTIR) spectroscopy (Nicolet 6700, Thermo Scientific, Shanghai, China). In the end, a soil sample from each pot was taken, air-dried, crushed, and passed through a 2 mm sieve. The Pb, Cd, Zn, and Cu metals were extracted to determine the bioavailable form using the toxicity characteristic leaching procedure (TCLP) method 1311 [29], which is suitable for polluted soils and their geochemical fractions using the European Union Community Bureau of Reference (BCR) procedure described below.

2.4. US EPA Extraction

The Environmental Protection Agency (EPA) classifies the TCLP as a determinant of the hazardousness and non-hazardousness of soil pollutants to determine the appropriate way to manage soils showing hazardous characteristics. Soil stabilization in the field before disposal can save the generator a great deal of money for transporting and disposing of hazardous waste. US EPA extraction was done by adding 20 mL of unbuffered glacial acetic acid (pH 2.88) to 1 gram of soil sample and the mixture was shaken for 18 h at 30 rpm and centrifuged at 3000 rpm for 30 minutes. The digested eluent was filtered and the HMs

in the extract were determined using an atomic absorption spectrometer (AA 800, Perkin Elmer Co. 14775 E Hinsdale Ave, Centennial, CO, USA).

2.5. Sequential Extraction Procedure (SEP)

An SEP was carried out using the BCR to examine the redistribution of Pb, Cd, Zn, and Cu as described by [30]. After, 1 g of each soil material was inserted into a 100 mL polycarbonate tube and the following steps were carried out for SEP: the acid-soluble fraction using 0.11 M acetic acid, the Fe/Mn oxide bound fraction using 0.1 M hydroxylamine hydrochloride (pH 2), the organic matter bound fraction using 30% *w/v* H_2O_2 and 1 M NH_4OAc (pH 2), and the residual fraction using HNO_3-HF-$HClO_4$. The concentrations of these metal fractions were measured using an atomic absorption spectrometer (AA 800, Perkin Elmer Co., 14775 E Hinsdale Ave, Centennial, CO, USA).

2.6. Quality Control

All the chemicals used in the present study were of analytical grade and purchased from Sigma Aldrich, St. Louis, MO, USA, and Merck, Munich, Germany. Standard procedures and protocols (US EPA) were followed for the extraction of different heavy metal fractions.

2.7. Statistical Analysis

The experimental design was a randomized complete block design with three replicates. The analysis of variance (ANOVA) and Duncan multiple range tests at a 5% level of probability were used to test the significance of differences between the treatments. The relation between metal forms and treatments was analyzed with principal component analysis (PCA) using Origin Pro 2018.

3. Results

3.1. Biochar Characterization

According to SEM-EDS analysis of the garden waste biochar at different pyrolysis temperatures (GB_{400} and GB_{600}), the carbon contents were higher in GB_{600} than in GB_{400}, whereas the opposite trend was noticed for the oxygen content.

The relative contents of P, Si, K, Mg, and Ca in GB_{400} were higher compared to those in GB_{600} (Figure 1). In addition, GB_{600} reached higher alkalinity than GB_{400} (Table 1). The O/C ratios of GB_{400} were higher than those of GB_{600} at 0.57 and 0.33, respectively. The FTIR analysis of GB biochars is shown in Figure 2. Hydroxyl (-OH), carbonyl or carboxyl (C=O), aromatic (C-H), and Si-O functional groups in GB_{400} were more stretched than those in GB_{600}, proving the ability of low-temperature pyrolyzed biochar to reduce heavy metal content.

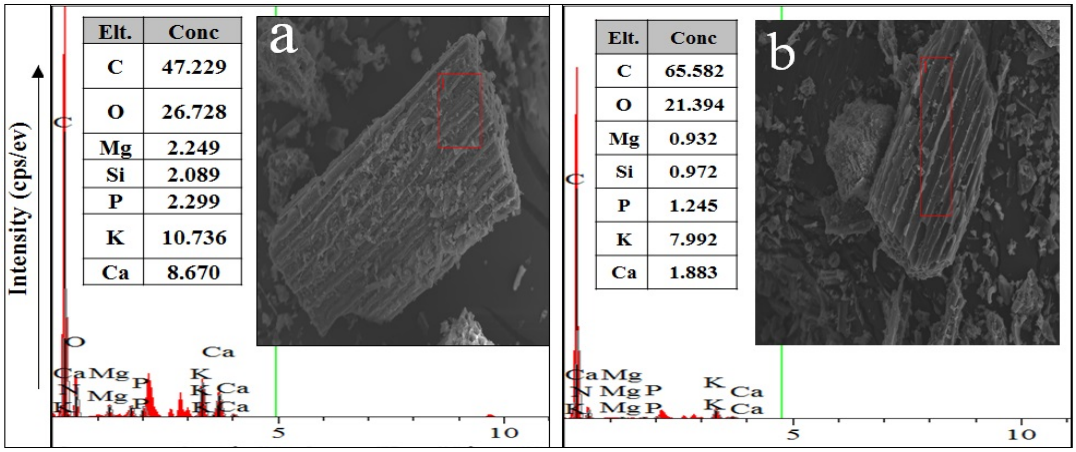

Figure 1. Scanning electron micrographs of a garden waste biochar pyrolyzed at 400 °C (GB_{400}) (**a**) and garden waste biochar at 600 °C (GB_{600}) (**b**), including the energy-dispersive X-ray spectra (EDS).

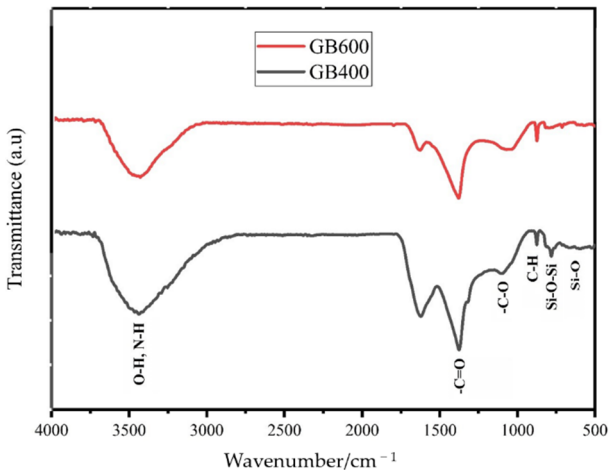

Figure 2. Fourier-transform infrared (FTIR) spectroscopy of garden waste biochar pyrolyzed at 400 °C (GB_{400}) and 600 °C (GB_{600}).

3.2. Soil Properties

Biochar types and their application levels significantly ($p < 0.05$) increased all soil properties in comparison to the control (Table 2). The highest rate of GB_{400} and GB_{600} increased the OM content by about 1.30 and 1.02 times more, respectively, than the untreated one. In the soil reaction (pH), a magnitude increase was observed with the highest level of both types. Except for the level of 2% GB_{400}, the electrical conductivity values (EC) were raised gradually according to the biochar type and its application rate.

Table 2. Organic matter (OM, gkg^{-1}), soil reaction (pH), and electrical conductivity (EC, dSm^{-1}) as affected by biochar application.

Biochar Treatment	Biochar Rate (%)	OM (g kg^{-1})	pH (1:2.5)	EC (1:10)
CK	0	23.7 ± 0.09^{g}	5.39 ± 0.02^{h}	0.45 ± 0.05^{f}
GB_{400}	2	33.8 ± 0.31^{f}	6.16 ± 0.10^{d}	0.33 ± 0.10^{g}
	4	$49.8 \pm 0.12^{c,d}$	7.04 ± 0.25^{b}	$0.60 \pm 0.01^{c,d}$
	6	$55.2 \pm 0.48^{a,b}$	7.27 ± 0.30^{a}	$0.62 \pm 0.04^{b,c}$
GB_{600}	2	33.8 ± 0.39^{f}	6.15 ± 0.12^{d}	0.54 ± 0.07^{e}
	4	43.6 ± 0.40^{e}	7.02 ± 0.01^{b}	$0.56 \pm 0.02^{d,e}$
	6	48.0 ± 0.22^{d}	7.26 ± 0.29^{a}	$0.64 \pm 0.03^{a,b,c}$

CK, control, no biochar application; GB, garden waste biochar pyrolyzed at 400 °C (GB_{400}) and 600 °C (GB_{600}) at rates of 2, 4, and 6%. The different letters indicate a significant difference between the biochar treatments ($p < 0.05$). All values are the means of three replicates.

3.3. Heavy Metal Mobility and Redistribution

3.3.1. TCLP-Extractable Metals

Contaminated soil requires special management according to its content of hazardous pollutants and their risk level, which is determined by the toxicity characteristic leaching procedure (TCLP) methods approved by the USEPA. In general, there were remarkable changes in HM concentration after biochar application compared to the untreated pots. The TCLP-extractable metals of Pb, Cd, Zn, and Cu significantly decreased after biochar application (Figure 3).

The noticeable decreases varied with biochar application rate and pyrolysis temperature. Generally, the garden waste biochar pyrolyzed at 400 °C was more effective than that pyrolyzed at 600 °C, especially at a high application rate (6%). The TCLP-extractable metals decreased by 67.76, 49.95, 38.43, and 63.99% for Pb, Cd, Zn, and Cu, respectively, using GB_{400} at a 6% application rate compared to the control. The corresponding reductions were 57.89, 40.05, 28.64, and 55.64%, respectively, for GB_{600} at a 6% application rate. In addition, Figure 4 illustrates the principal component analysis (PCA), which shows that the total

variance was 99.5%, with the PC1 explaining 98.7% of the variance, which confirms that the biochar treatments had a positive effect on reducing the TCLP-extractable metals.

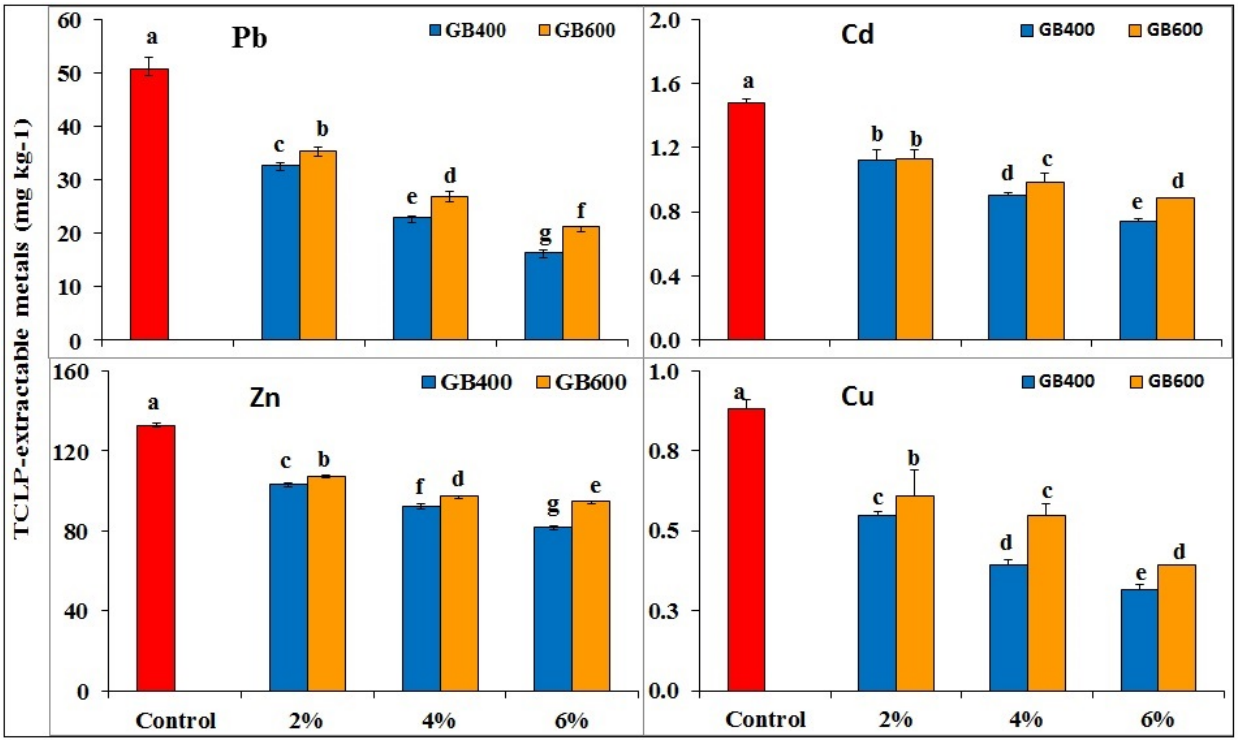

Figure 3. Impact of biochar additives (garden waste biochar pyrolyzed at 400 °C (GB_{400}) and 600 °C (GB_{600})) at 2, 4, and 6% rates on the immobilization of TCLP-extractable metals (mg kg^{-1}) in contaminated soils. Values in a given column followed by the same letter are not significantly different ($p < 0.05$). All values are the means of three replicates.

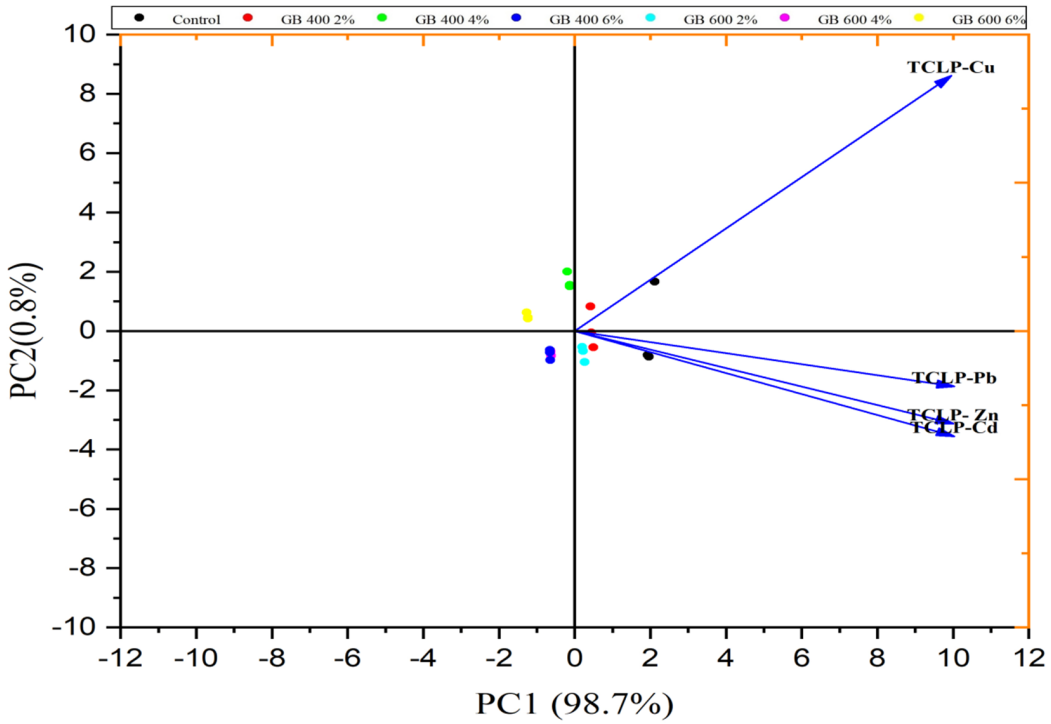

Figure 4. Principal component analysis (PCA) of the toxicity characteristic leaching procedure (TCLP-extractable) of Pb, Cd, Zn, and Cu metals after biochar additives (garden waste biochar pyrolyzed at 400 °C (GB_{400}) and 600 °C (GB_{600})) at 2, 4, and 6% rates. PC: principal components.

3.3.2. Acid-Soluble Fraction

The acid extractable fractions of Pb, Cd, Zn, and Cu were significantly decreased by biochar application (Table 3). The obvious reduction of these metal fractions was evident by increasing the biochar application rate and the metal species (Figure 5).

Table 3. Acid extractable metal concentration of Pb, Cd, Zn, and Cu (mg kg^{-1}) after biochar application.

Biochar Treatment	Biochar Rate (%)	Pb	Cd	Zn	Cu
CK	0	137.79 ± 1 ^{a}	1.83 ± 0.14 ^{a}	168.01 ± 3 ^{a}	2.01 ± 0.13 ^{a}
GB_{400}	2	119.84 ± 2 ^{c}	1.54 ±0.15 ^{b}	150.70 ± 3 ^{b}	1.28 ± 0.01 ^{b}
	4	95.01 ± 1 ^{e}	1.44 ± 0.10 ^{c}	146.82 ± 13 ^{b}	0.91 ± 0.05 ^{c}
	6	66.77 ± 3 ^{g}	1.38 ± 0.08 ^{c}	141.68 ± 1 ^{c}	0.52 ± 0.02 ^{d}
GB_{600}	2	125.16 ± 3 ^{b}	1.59± 0.07 ^{b}	153.24 ± 2 ^{b}	1.28 ± 0.01 ^{b}
	4	103.93 ± 5 ^{d}	1.44 ± 0.10 ^{c}	152.55 ± 3 ^{b}	0.90 ± 0.01 ^{c}
	6	85.69 ± 5 ^{f}	1.42 ± 0.09 ^{c}	151.56 ± 1 ^{b}	0.52 ± 0.02 ^{d}

CK, control, no biochar application; GB, garden waste biochar pyrolyzed at 400 °C (GB_{400}) and 600 °C (GB_{600}) at rates of 2, 4 and 6%. The different letters indicate a significant difference between the biochar treatments ($p < 0.05$). All values are the means of three replicates.

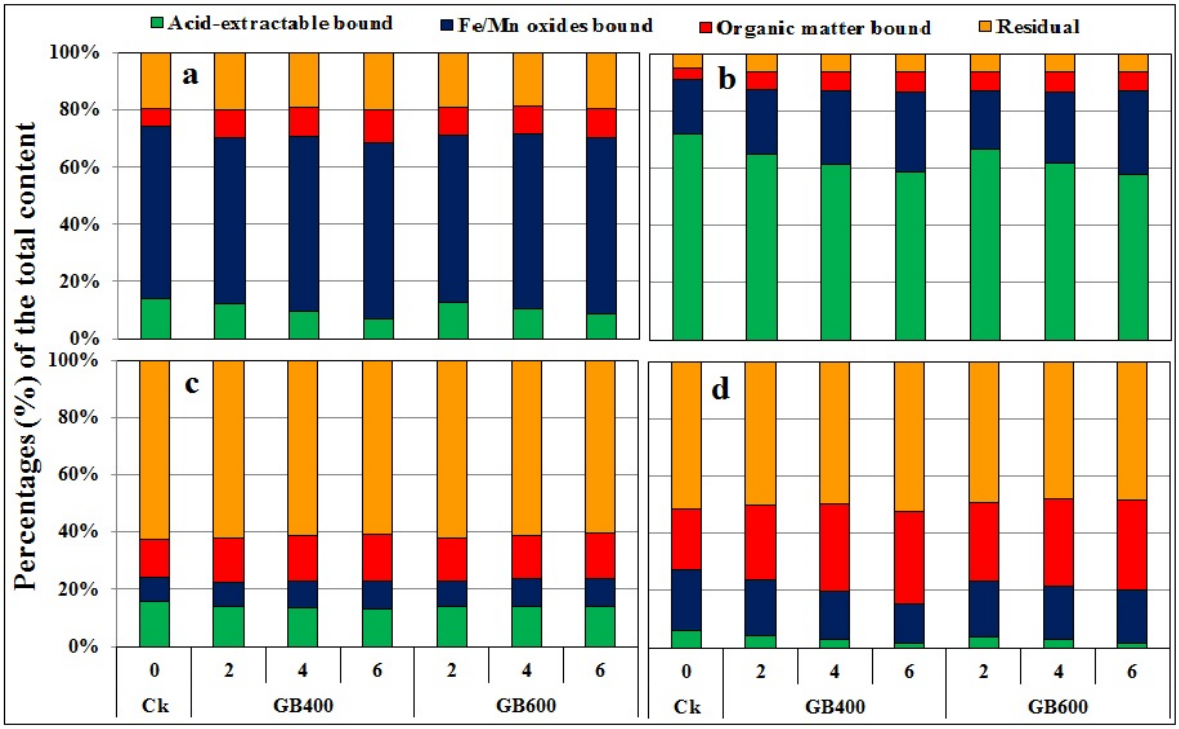

Figure 5. Redistribution of Pb (**a**), Cd (**b**), Zn (**c**), and Cu (**d**) (as percentages of the total content) among the chemical forms of the studied soils treated with garden waste biochar pyrolyzed at 400 °C (GB_{400}) and 600 °C (GB_{600}) at rates of 2, 4 and 6%. All values are the means of three replicates.

Copper (Cu) was the metal most affected by biochar addition, followed by lead (Pb), the reductions of which were 74.13 and 51.54%, respectively, at 6% of GB_{400} compared to the control treatment. GB_{400} was more effective in reducing the acid extractable fraction of Pb and Zn than GB_{600}. However, there were no significant differences between biochar levels in the cases of Cd and Cu. The acid extractable fraction of the total metal content represented 6.81 to 12.77% of Pb, 58.06 to 77.05% of Cd, 13.90 to 16.55% of Zn, and 1.53 to 5.91% of Cu depending on application levels and pyrolysis temperature. Although the cadmium content of the tested soil was the lowest compared to other metals, increased availability

may cause threats to the ecosystem due to high toxicity. Therefore, the mobility of target metals was in the ascending order of Cu > Pb > Zn > Cd.

3.3.3. Oxide-Bound Fraction

The Fe/Mn oxide-bound fractions of Cu were significantly reduced by biochar application and the reduction was more pronounced at a high addition rate (Table 4). There was an irregular trend in the case of Pb in the oxide-bound fraction with the biochar application level. The highest amount of Pb bound to iron and manganese oxides was recorded with GB_{600}, followed by GB_{400} at a 4% level (Table 4). A larger portion of Fe/Mn oxide-bound Pb was recorded compared to other metals, which confirms its affinity to binding those oxides (Figure 5). In the case of Cd and Zn, the oxide-bound fraction was significantly increased ($p < 0.05$) with all biochar additives. It showed a gradual increase depending on the application levels at different pyrolysis temperatures, whereas the opposite trend was observed with Cu.

Table 4. Iron and manganese oxide-bound concentration of Pb, Cd, Zn, and Cu (mg kg^{-1}) after biochar application.

Biochar Treatment	Biochar Rate (%)	Pb	Cd	Zn	Cu
CK	0	$602.33 \pm 10^{a,b}$	0.494 ± 0.013^{f}	85.83 ± 4^{c}	6.94 ± 0.71^{a}
GB_{400}	2	$561.02 \pm 6^{d,c}$	0.537 ± 0.006^{e}	93.66 ± 1^{b}	6.25 ± 0.01^{b}
	4	614.15 ± 6^{a}	0.602 ± 0.007^{c}	99.50 ± 1^{a}	5.48 ± 0.01^{c}
	6	$593.48 \pm 13^{a,b}$	0.669 ± 0.010^{b}	103.42 ± 3^{a}	4.34 ± 0.01^{d}
GB_{600}	2	582.65 ± 1^{b}	0.486 ± 0.013^{f}	94.22 ± 3^{b}	$6.63 \pm 0.02^{a,b}$
	4	615.87 ± 18^{a}	0.569 ± 0.078^{d}	101.70 ± 3^{a}	6.38 ± 0.44^{b}
	6	$592.60 \pm 10^{a,b}$	0.706 ± 0.003^{a}	102.83 ± 10^{a}	6.39 ± 0.42^{b}

CK, control, no biochar application; GB, garden waste biochar pyrolyzed at 400 °C (GB_{400}) and 600 °C (GB_{600}) at rates of 2, 4, and 6%. The different letters indicate a significant difference between the biochar treatments ($p < 0.05$). All values are the means of three replicates.

3.3.4. Organic Matter Bound Fraction

Soil organic matter (SOM) content bound metals significantly increased with biochar application (Table 5). This increase was mostly at the expense of the acid fraction, and in part of the oxides bound (Figure 5). The organically bound Pb fraction increased up to 76.10% for GB_{400} at a high rate compared to the control. The GB_{400} and GB_{600} added at a high rate increased the organic bound Cd by 54.69 and 54.51%, respectively. The highest application of GB at 400 and 600 °C pyrolysis increased the OM bound fraction of Zn to reach 23.72 and 19.18%, respectively, over the control. The OM bound fraction of Cu increased by 49.07% due to adding 6% GB_{600}.

Table 5. Organic matter-bound concentration of Pb, Cd, Zn, and Cu (mg kg^{-1}) after biochar application.

Biochar Treatment	Biochar Rate (%)	Pb	Cd	Zn	Cu
CK	0	62.03 ± 1^{e}	0.104 ± 0.011^{c}	141.82 ± 1^{a}	7.34 ± 0.52^{e}
GB_{400}	2	96.30 ± 1^{d}	0.145 ± 0.014^{b}	168.09 ± 10^{a}	8.15 ± 0.05^{d}
	4	104.91 ± 2^{b}	0.156 ± 0.005^{a}	173.15 ± 5^{a}	9.81 ± 0.45^{b}
	6	109.24 ± 1^{a}	0.167 ± 0.015^{a}	175.46 ± 1^{a}	$10.32 \pm 0.88^{a,b}$
GB_{600}	2	96.64 ± 2^{d}	0.161 ± 0.007^{a}	160.48 ± 3^{a}	9.30 ± 0.05^{c}
	4	99.75 ± 1^{c}	0.163 ± 0.015^{a}	166.14 ± 12^{a}	$10.19 \pm 0.89^{a,b}$
	6	99.96 ± 3^{c}	0.167 ± 0.004^{a}	169.02 ± 9^{b}	10.70 ± 0.44^{a}

CK, control, no biochar application; GB, garden waste biochar pyrolyzed at 400 °C (GB_{400}) and 600 °C (GB_{600}) at rates of 2, 4, and 6%. The different letters indicate a significant difference between the biochar treatments ($p < 0.05$). All values are the means of three replicates.

3.3.5. Residual Metals

The residual fractions of the tested metals did not significantly change with the application of the tested biochars (Table 6). The highest portion (about 60%) of the residual fraction contained Zn, followed by Cu, Pb, and Cd (Figure 5). The residual fractions of Pb, Cd, Zn, and Cu varied from 19.09 to 20.06, from 5.37 to 6.31, from 63.42 to 66.11, and from 46.84 to 50.03%, respectively.

Table 6. Residual concentration of Pb, Cd, Zn, and Cu (mg kg^{-1}) after biochar application.

Biochar Treatment	Biochar Rate (%)	Pb	Cd	Zn	Cu
CK	0	196.61 ± 2 [a]	0.131 ± 0.010 [b]	664.67 ± 45 [a]	17.01 ± 0.31 [a]
GB_{400}	2	193.89 ± 8 [a]	0.148 ± 0.002 [a]	676.47 ± 16 [a]	15.93 ± 1.25 [a]
	4	193.55 ± 10 [a]	0.150 ± 0.001 [a]	665.08 ± 17 [a]	16.05 ± 0.93 [a]
	6	193.89 ± 26 [a]	0.148 ± 0.007 [a]	657.42 ± 25 [a]	16.81 ± 1.46 [a]
GB_{600}	2	193.06 ± 4 [a]	0.153 ± 0.012 [a]	673.63 ± 6 [a]	16.75± 0.22 [a]
	4	187.09 ± 5 [a]	0.151 ± 0.006 [a]	659.60 ± 5 [a]	16.11 ± 0.39 [a]
	6	188.25 ± 11 [a]	0.154 ± 0.001 [a]	646.27 ± 5 [a]	16.51 ± 1.38 [a]

CK, control, no biochar application; GB, garden waste biochar pyrolyzed at 400 °C (GB_{400}) and 600 °C (GB_{600}) at rates of 2, 4, and 6%. The different letters indicate a significant difference between the biochar treatments ($p < 0.05$). All values are the means of three replicates.

4. Discussion

4.1. Biochar Effect

The tested biochars had high organic matter content, salinity, and alkalinity (Table 1). Consequently, those parameters were high in the soil treated with biochar, and the increase was more evident with high rates of biochar application. These results were compatible with those obtained by [31–33]. The decrease in soil salinity values resulting from 2% GB_{400} may be attributable to salt adsorption by biochar, maintenance without an increase in soil solution, and/or downward movement of saline water resulting in a lower EC value [3,34–36]. It was found that garden biochars reduced toxic metal risk by stabilizing them in insoluble forms. GB_{400} and GB_{600} were effective in metal immobilization, especially GB_{400}. This may have been due to a high content of O, K, Ca, Mg, and P elementals as a contributing factor, which are linked to heavy metals ending with an insoluble form (Figure 1). These results are consistent with those obtained by [17,37–39]. They indicated that the biochar created HM complexation with various elementals of its structure, such as O, P, S, Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+} through cation exchange.

The HM mobility induced by 6% biochar application was lower than those of other levels (2 or 4%). Depending on these application rates, the decrease in the level of the studied metals may have been partly related to the increase in acidity values induced by biochar additives compared to the unamended soil. In other words, increasing biochar additions increased the cations and active groups, which decreased the extractable metal concentration by forming stable complexes. These results are consistent with those posted by [25,40]. They reported that biochar applications raised the pH of acid soils, increasing the adsorption and metal complexation on the biochar and consequently decreasing the metal mobility. However, in contaminated flooded soil, [41] pointed out that the extractable Cd, Pb, and Zn concentration decreased after a three-year incubation with biochar application. In addition, [42] confirmed that Cd concentration extracted with $CaCl_2$ from an artificially contaminated soil with 50 mg kg^{-1} Cd was significantly lower at a 5% biochar application level than at a 1% level. An incubation experiment carried out for one year by [43] showed that increasing the biochar addition of the used biochar decreased HMs, which was greatly significantly ($p < 0.01$) and associated with soil pH. The $CaCl_2$ and DTPA extractable metals were lower at 5% than at 1% level of biochar application to a contaminated soil [44].

4.2. Pyrolysis Effect

The results show that garden waste biochars (GB) produced at low (400 °C) or high (600 °C) temperatures caused a reduction in concentration of the tested metals. The effectiveness of GB in reducing the tested HMs depended upon the pyrolysis temperature, since GB_{400} was more efficient than GB_{600}. The PCA data also confirmed that GB_{400} was the most effective treatment (Figure 4). This may be attributed to the higher elemental content (Figure 1), which increased the chemical and/or physical adsorption on the biochar surface. In this regard, [45] reported that the number of bound metals representing functional groups (FG) is found in biological indices obtained at low temperatures (300 and 500 °C). In addition, pyrolysis at a low temperature and the incremental release of available P, K, and Ca is related to high Pb stabilization [46]. These results illustrate that lower temperature pyrolysis leads to the formation of outer-sphere complexes resulting in more short-term metal immobilization. Therefore, biochars produced at a higher temperature may result in negative surface charges that should make the metal be stable longer but more weakly absorbed to biochar surfaces. On the other hand, the lower-temperature ones have more negatively charged surfaces that bind HMs powerfully, but decrease with time [47].

4.3. Metal Mobility and Redistribution

Soil treated with biochar was significantly more efficient in reducing Pb, Cd, Zn, and Cu concentrations by TCLP and acid extractable fractions than the untreated one (Table 3 and Figure 3). Comparable results were observed by [46,48]. They indicated that the addition of cottonseed hull biochar to the contaminated soil resulted in reducing the TCLP-extractable Pb, Cu, and Zn after one week. In addition, [49] also showed that the biochar addition significantly decreased the acid fraction of Pb, Cd, and Cu. Based on the European Union Community Bureau of Reference (BCR) method, the concentrations of the acid extractable metals are arranged in descending order of Cd > Zn > Pb > Cu. These results are mainly attributed to soil pH (Table 2) and the element's characteristics, such as the affinity of ligand-exchange sites on oxides and organic matter. These results are consistent with those obtained by [17], who found that the acid extractable metal fractions (F1) using BCR methods were ranked in the order of F1: Ni > Mn > Cd > Zn > Pb > Cr > Co > Cu. These decreases in HM concentration might be due to the precipitation as a result of increasing pH value, which is associated with increasing biochar application level, especially in acid soil. The biochar-amended soil showed evident decreases in Fe/Mn oxides bound to Pb and Cu, especially to Pb, whereas generally, it increased in the case of Cd and Zn compared to the control. This result may be due to the metal characteristics and the affinity of Mn oxides for lead and copper. Ref. [50] found that Pb^{2+} had the greatest adsorption affinity among the tested heavy metals. On other hand, biochar application significantly increased OM-bound metal fractions compared with the control. However, these decreases in the acid extractable metals were at the expense of increased OM-bound metal fraction. However, the increase in the OM-bound metal fraction due to the use of GB was dependent on the application level and pyrolysis temperature. These results are compatible with those obtained by [11,51]. They indicated that biochar application caused an increase in the metal fraction bound to the organic matter. Heavy metals can form stable organic complexes adsorbed on biochar surfaces, causing immobilization and reduction in their concentrations in the soil solution [52].

4.4. Heavy Metal Immobilization Mechanisms

Biochar has the ability to immobilize organic contaminants [53] and HMs [54] through different mechanisms, such as physical adsorption [38]; chemical adsorption with Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, and S [16,37,38]; complexation with Pb^{2+} and Cu^{2+} [4,37]; the formation of precipitates through phosphate compounds [4,55,56]; and precipitation as a result of pH elevation [13,57]. So far, the extent to which one or more of these different mechanics contributes to HM immobilization by different feedstock is still unknown, although many researchers have reported that it is mostly affected by soil reaction (pH) [41,58]. GB

pyrolyzed at 400 °C was more efficient in HM immobilization. This might have been due to the functional groups of GB as well as its higher elemental composition content (Figure 1). In the sequential extraction method, biochar addition reduced the metal portion associated with acetic acid and realized the organic matter binding, which indicates that GB_{400} was more effective. The reduction in acid extractable metals at the expense of an increased organic matter bound-metal fraction (Figure 5) led to the formation of more stable compounds and thus, HM immobilization as a result of biochar application. Although the alkalinity (11.00) and electrical conductivity (5.50) of GB_{400} was lower than GB_{600}, the high elemental composition (Figure 1) may explain the greater decrease in HM mobility.

5. Conclusions

Differences in heavy metal immobilization induced by biochar application indicate that reducing their solubility mainly depends on soil pH, organic matter content, type of metal, and its ability to interact with the biochar surface. In addition, pyrolysis temperature, application level, and pH values are important factors in reducing heavy metals' solubility. Garden biochar pyrolyzed at 400 °C (GB_{400}) was more efficient than that pyrolyzed at 600 °C (GB_{600}) in reducing HM risks and transformations. An increase in the organic bound and Fe/Mn oxides versus a sharp decrease in the acid-soluble fraction confirms that transformation among the different forms had the superlative effect on reducing the potential risks of the tested HMs. A clear decline in the soluble fraction of tested HMs was matched by an increasing soil reaction, especially with high levels of biochar addition. An increase in soil organic matter content caused an evident reduction in HM solubility and therefore, environmental risks. The difference in the soluble amount from one metal to another confirms the ability of each metal to be attached to a specific soil portion. Pyrolysis at a low temperature is more effective than at a high temperature in immobilizing HMs. It is worth mentioning that higher concentrations of 6% biochar mixture are more effective in reducing HM mobilization under acidic soil conditions. Despite the variety of the biochar rates used (2, 4, and 6%), the reduction of heavy metals in terms of its relationship to the addition rate still requires more studies on this soil exclusively to evaluate the effect of different biochar additives on soil properties and HM reduction. This study proves that garden waste biochar is a promising material in reducing heavy metal solubility in a manner that reduces its hazardous environmental effects.

Author Contributions: Conceptualization, M.A. and Z.L.; Data curation, M.A., M.M.E.-S. and X.L.; Formal analysis, M.A., M.M.E.-S. and S.K.M.; Funding acquisition, K.H.; Investigation, M.A.; Methodology, M.A.; Re-sources, X.L. and Z.L.; Software, M.M.E.-S. and Z.L.; Supervision, Z.L.; Writing—original draft, M.A. and M.M.E.-S.; Writing—review & editing, M.A., X.L., S.K.M., A.D. and K.H. All authors have read and agreed to the published version of the manuscript.

Funding: The authors would like to acknowledge Taif University Researchers Supporting Project number (TURSP-2020/94), Taif University, Taif, Saudi Arabia.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: This study was financially supported by the Agricultural competitive industry discipline team building project of Guangdong Academy of Agricultural Sciences (202120TD); National Natural Science Foundation of China (41571313, 41401353); Science and Technology Planning Project of Guangdong Province. China (2019B121201003, 2020A1414010312, 2020B1212060055). The authors would like to acknowledge Taif University Researchers Supporting Project number (TURSP-2020/94), Taif University, Taif, Saudi Arabia. The authors thank Ayman El Sabagh and Ibrahim Al-Ashkar for their contributions to the editing and improvement of the discussion of results for the paper.

Conflicts of Interest: All authors declare that there is no conflict of interest.

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