Chapter

The Use of Biochar as a Soil Amendment to Reduce Potentially Toxic Metals (PTMs) Phytoavailability

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Abstract

The contamination of potentially toxic metals (PTMs) is widespread in the world and has negatively affected plants, humans, soil health, and environmental quality. Some metals are essential plant nutrients but they are also toxic to vegetation and aquatic live when present in high concentrations, such as Cu, Mn and Zn. Others (e.g., Pb, Cd, Cr, and As) are potential toxic metals for all organisms, and are not needed (or are toxic) for plant growth. This chapter summarizes the use of readily available biochars (BCs) to reduce PTMs phytoavailability in soils thus improving crop yields and to minimize its impact on the environment. The physicochemical and morphological properties of BCs as affected by feedstock sources and pyrolysis temperatures are discussed. The effectiveness of biochar rates on plant growth and metal fractions are also highlighted. Biochar has the potential to be used as a viable bioproduct for the remediation of contaminated soils since it reduces the phytoavailability of PTMs pollutants. Biochars produced from different feedstocks and at different pyrolysis temperatures present highly heterogeneous physicochemical and morphological properties, which can affect the effectiveness in the remediation of PTMs contaminated soils. Therefore, potential technologies need to be developed and research gaps still need to be overcome to optimize the use of BCs as a feasible alternative for remediation of metal contaminated soils.

Keywords: soil remediation, biochar amendment, potentially toxic metals, phytoavailability, immobilization, soil health

1. Introduction

Biochar is a carbon-rich by-product produced from the thermochemical conversion of biomass feedstock under partial or total absence of oxygen [1, 2]. Feedstocks used in biochar (BC) production are mostly wood, municipal and agriculture wastes [3–6]. Amending soil with biochar has received increased attention as a method for carbon sequestration in soils, thereby reducing carbon dioxide (CO_2) emissions [7–9] and improving soil quality due to the vital role of carbon (C) in soil physical, chemical and biological processes [10].

Amending soil with biochar has been practiced for a long time. The high fertility of anthropogenic dark earth soils known as 'Terra Preta de Indio' in the Amazon basin has been related to the high content of charred materials [11–13]. Historically, the source of char in these soils has been considered as a disposal of charcoal from domestic fires and the practice of slash and char agriculture by Pre-Columbian Amazonian Indians [11, 14]. Hence, these soils have remained fertile and rich in biochar derived C stock for hundreds to thousands of years after they were abandoned.

In addition to the role of biochar in increasing the C sequestration and influencing the reduction of CO_2 emissions, biochar has been shown to enhance soil quality and to stabilize PTMs [15]. Biochar has a potential benefit for improving soil fertility [16, 17], improving soil properties such as pH [11–13, 18], cation exchange capacity (CEC) and water holding capacity [19], enhancing plant growth [20], and reducing nutrient leaching losses [21]. The significant amount of calcium (and magnesium) carbonate ($Ca/MgCO_3$) in BCs enables them to function as lime materials providing Ca and Mg to plants and neutralizing acidity when applied to acid soils.

The role of biochar in improving soil pH, organic carbon (OC), and CEC was also highlighted by [16]. Moreover, biochar can immobilize PTMs (immobilization is the reduction of the potential migration of PTMs to plants, or reduction of phytoavailability) such as cadmium (Cd), lead (Pb), and zinc (Zn) and thereby to reduce the phytoavailability of PTMs (concentration of PTMs in plant parts, or contents of PTMs in soils available to plants) to plants in contaminated soils, notably because it raises the soil pH [18, 22] and increases CEC and OC [23]. Many studies also found biochar application promotes the ability to remove organic contaminants [24, 25]. Because of its porous structure and diverse functional groups [26], biochar has been widely used in the field of agriculture and environmental protection [27] due to its ability to improve soil health and crop yields, and sequestering carbon, immobilizing PTMs and adsorbing organic pollutants such as polycyclic aromatic hydrocarbons (PAHs).

For these reasons, studies on biochar land-application have exponentially increased in the last 20 years (**Figure 1**). During the same period (1999–2018), the word 'potentially toxic metal' or 'heavy metal' places itself in the **top 5** within the 25 keywords used in biochar researches, numbering **308** publications [6]. Therefore, this chapter is to provide a summary of the most recent studies on biochar use to improve soil quality and to immobilize the phytoavailability of PTMs to plants of agricultural importance. The main goal is to improve our

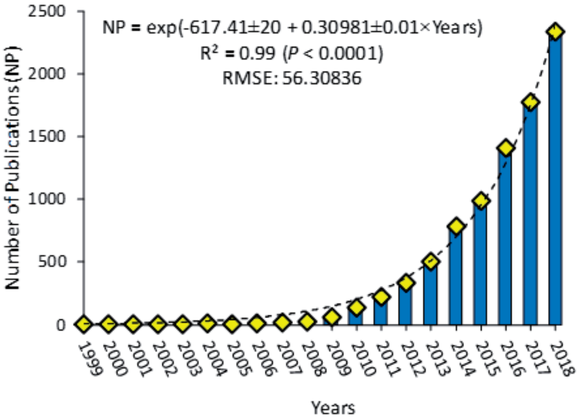

Figure 1.
Number of publications (NP) of biochar studies since 1999 (adapted from [6]). RMSE: Root mean square error value of the exponential model adopted.

understanding of biochar production and application as a soil remediation technique and to serve as the basis for future research work.

2. Biochar increases soil pH and soil organic carbon content and affects PTMs phytoavailability

The effects of pH rising in soils are significantly influenced by biochar addition more than by other practices such as liming [28]. **Table 1** shows some of the main characteristics of BCs (pH included) as affected by feedstock sources and pyrolysis temperature. Biochar is superior to lime to remediate PTMs-polluted areas, mainly because acidic conditions can lead to the leaching of metals and threatening of groundwater [28]. Biochars can supply OC and raise soil pH, but lime only increases soil pH. Hence, poultry litter-derived biochar (PLB) proves itself as very effective in immobilizing Cd, even under strong acidic conditions, thus preventing Cd leaching

Biochar feedstock	Pyrolysis temperature (°C)	Water (wt%)	TC (wt%)	TOC (wt%)	TN (wt%)	pH	Reference
Wood of 'Quaresmeira' (*Tibouchina arborea*)	330	55	82	80	—	9.7	[13]
Poultry litter	450	—	38	—	2	9.9	[16]
	550	—	33	—	0.85	13	
Miscanthus (Miscanthus × giganteus) straw	600	—	53.5	—	0.31	10	[18]
1-Switchgrass straw	500	—	23.7	—	0.8	9.4	[19]
2-Anaerobically digested fiber		—	25	—	0.85	9.3	
3-Softwood bark		—	28.4	—	0.14	7.6	
4-Wood pellets		—	28.2	—	0.05	7.2	
1-Swicthgrass	350	1.4	42.6	—	0.9	5.2	[23]
	700	1.7	31.4	—	0.7	10	
2-Poultry litter	350	2.7	38.4	—	4.1	7.4	
	700	3.9	27.8	—	1.6	10	
1-Pig manure	350	—	31.6	—	3.8	8.3	[25]
	700	—	25.2	—	2.1	9.5	
2-Deashed pig manure-biochar	350	—	66.7	—	7.6	6.2	
	700	—	74.2	—	5	6.4	
1-Poultry litter	400	—	16.8	—	1.4	10	[28]
2-Eucalyptus	600	—	81	—	1.1	10.4	

TC: total carbon. TOC: total organic carbon. TN: total nitrogen. "—": not given.

Table 1.
Summary of some biochar properties as affected by feedstock sources and pyrolysis temperature.

to the groundwater [28]. Besides raising the soil pH, the enhanced OC provided by biochar addition contributes to a decrease in the phytoavailability of PTMs by reducing metal mobility due to bonding metals into more stable fractions [29, 30], such as organic matter-bound and/or highly stable organic complexes which are not readily dissolved by water. The increase of both pH and OC also contributes to a higher CEC, then resulting in a higher PTMs adsorption [31].

The application of orchard prune-derived biochar (OPBC) to mine tailings reduced phytoavailable (DTPA-extractable) concentrations of Pb, Cd, and Zn [32]. Rice straw-derived biochar reduced Cd concentration in the plant available soil fraction grown in a greenhouse [30]. Biochar addition also showed a potential in reducing Cd and Pb accumulation in ryegrass (*Lolium perenne*) shoots, thus presenting a viable option for safe cultivation in PTMs-polluted soils [29]. Recent studies [22, 33] have found the ability of biochar to reduce the phytoavailability of PTMs (Cu, Zn, Pb, Cd, Mn, and Ni) to ryegrasses. Particularly, the study conducted by [22] elucidated that soil pH and OC increases as a function of biochar application rates played a big role in PTMs (Zn, Pb, and Cd) immobilization, mainly by forming stable (and undissolved) complexes with hydroxyls (OH^-) ($Zn/Pb/Cd_x(OH)_y$) and surface functional groups, respectively. **Figure 2** summarizes their findings and illustrates the importance of biochar application as a soil remediation technique. In another study, the concentrations of Cu, Pb, and Zn decreased as the rates of BCs applied increased, with a significant effect for amendments >1% w/w applied. Especially, the phytoavailability of PTMs decreases gradually with time when the soil is amended by 5% or 10% w/w of biochar [18].

It has been shown that the addition of sugar cane bagasse-derived BC (SCBC) decreased the phytoavailable Pb fraction by 97%, and that the PTM uptake by maize plants decreased with increasing the level of applied BC [34]. The authors attributed such results to an enhancement of soil pH and soil organic carbon (SOC) because of BC addition. In addition, an unpublished work conducted by Antonangelo and Zhang has also revealed how impacting is the increase of soil pH and SOC, as biochar application rates increase, on PTMs (Zn, Pb and Cd) mobility. The study was carried out with no plants and the application rates of poultry litter- (PLB) and switchgrass-derived biochar (SGB) ranged from 0 to 8% w/w

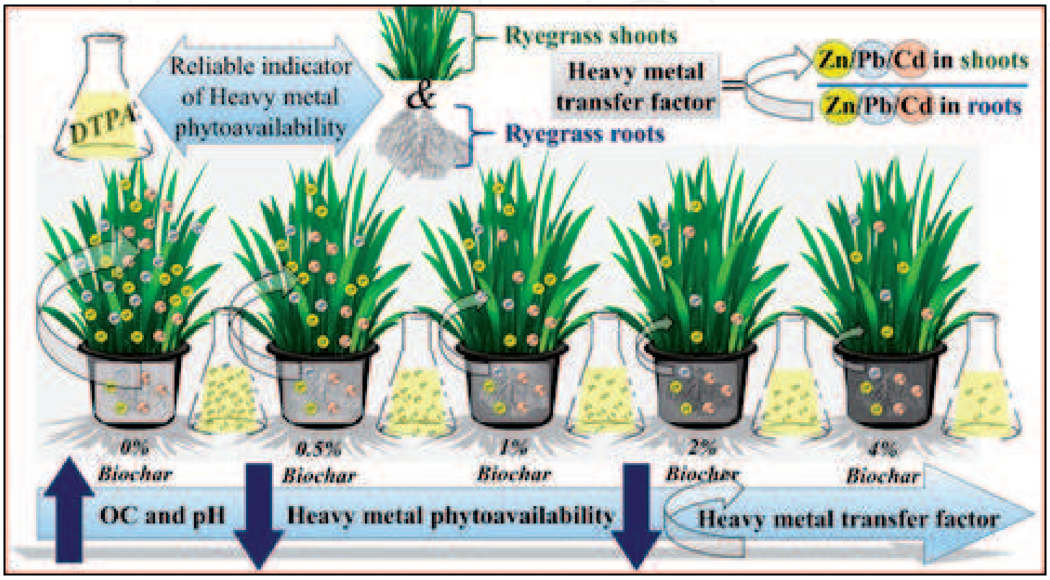

Figure 2.
Potentially toxic metal (heavy metal) immobilization to ryegrass shoots and roots as a function of biochar application rates. Diagram was created from the work of [22].

in multi-metal contaminated soil. Potentially toxic metal phytoavailability was assessed by using two extraction methods (NH_4NO_3 and DTPTA) after 10 weeks of soil + biochar incubation under laboratory room temperatures. The results of PTMs contents in the extracts and SOC (%) as a function of biochar application rates are summarized in **Figures 3** and **4**, and **Table 2**. The pH increase from 6.5 to 8.0, as shown in **Figure 3**, is a consequence of the increased BCs (SGB and PLB) application rates from 0 to 8%, so is the SOC increase, as shown in **Figure 4**. **Table 2** highlights the significant negative correlations (inverse relationship) of pH and SOC (independent variables) with phytoavailable PTMs in the filtered extracts (dependent variables).

The immobilization of Cu, Pb, Cd, and Ni by BCs was attributed to the quantity of surface oxygen-functional groups, which is directly related to the amount of carbon (C) present in the biochar composition [35]. Uchimiya et al. [36] reported that biochar enhanced Cu sorption in a sandy loam soil primarily by cation exchange mechanism, enhanced by the soil C increase. Hence, biochar addition increased the sorption capacity of the soil matrix for both organic and inorganic contaminants [37]. However, BCs may favor the availability of some PTMs such

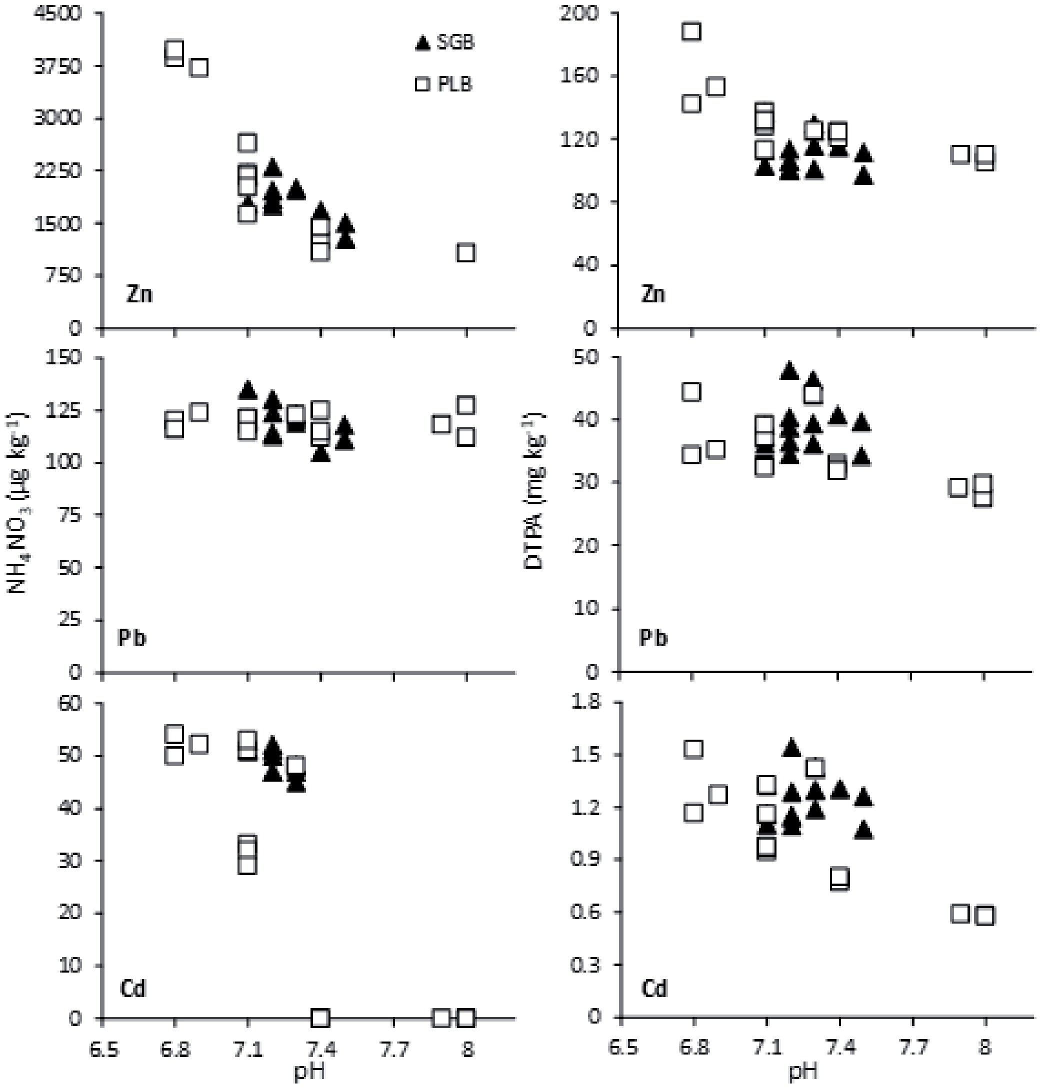

Figure 3.
Relationship between pH and metal concentrations in NH_4NO_3 and DTPA extracts after 10 weeks of biochar incubation. Points were plotted from the whole dataset of measurements. One outlier from three replicates (n = 3) was removed, when detected, by using IML and UNIVARIATE (ROBUSTSCALE) procedures of the SAS program. pH ranged from 6.5 to 8.0 as biochars (SGB and PLB) application rates increased from 0 to 8% w/w of biochar.

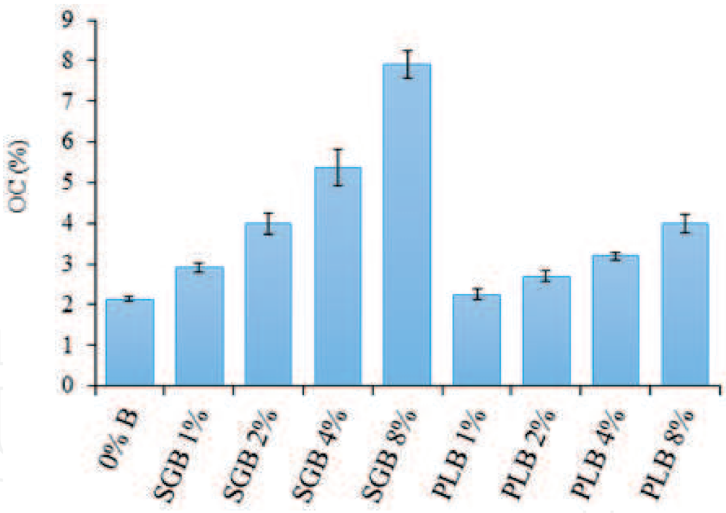

Figure 4.
Soil organic carbon (OC%) changes due to biochar (SGB and PLB) application rates after 10 weeks of incubation. Bars represent the standard deviation of the mean (n = 3) results are significant at $P < 0.01$ *(Tukey test).*

Soil attribute	SGB	PLB	SGB + PLB	SGB	PLB	SGB + PLB
		Zn (NH_4NO_3)			Zn (DTPA)	
pH	-0.75^{**}	-0.82^{***}	-0.81^{***}	-0.15^{NS}	-0.76^{***}	-0.55^{**}
OC	-0.79^{**}	-0.74^{**}	-0.43^{*}	-0.31^{NS}	-0.60^{*}	-0.47^{*}
		Pb (NH_4NO_3)			Pb (DTPA)	
pH	-0.55^{*}	-0.05^{NS}	-0.16^{NS}	0.03^{NS}	-0.63^{*}	-0.44^{*}
OC	-0.64^{*}	-0.11^{NS}	-0.46^{*}	-0.12^{NS}	-0.77^{**}	0.10^{NS}
		Cd (NH_4NO_3)			Cd (DTPA)	
pH	-0.91^{***}	-0.82^{***}	-0.72^{***}	0.04^{NS}	-0.83^{***}	-0.66^{***}
OC	-0.91^{***}	-0.91^{***}	-0.01^{NS}	-0.11^{NS}	-0.92^{***}	0.06^{NS}

**: $P < 0.05$; **: $P < 0.01$; ***: $P < 0.001$; NS: non-significant ($P > 0.05$). The R-values were calculated from the whole dataset of measurements. SGB + PLB: two biochar treated soils. One outlier from three replicates (n = 3) was removed, when detected, by using IML and UNIVARIATE (ROBUSTSCALE) procedures of SAS program.*

Table 2.
Pearson correlation coefficient (R) between metal extracted from NH_4NO_3 or DTPA and soil attributes (pH and organic carbon-OC) after 10 weeks of soil+biochar (SGB and PLB) incubation.

as arsenic (As). The addition of sugar cane bagasse-derived BC (SCBC) stabilized Pb but accelerated the desorption of arsenic (As); consequently, increased its availability [38]. That is probably a result of charge repulsion between the negatively charged SCBC and the arsenate anion (AsO_4^{3-}).

3. The effect of biochar feedstock sources on PTMs phytoavailability

While investigating the effects of chicken manure (CMB) and greenwaste biochar (GWB), both produced at 550°C (pyrolysis temperature), on the immobilization and phytoavailability of Cd, Cu and Pb in metal-spiked and multi-metal contaminated soils, [39] found that both BCs significantly decreased Cd and Pb mobility, mostly by modifying those PTMs from the easily exchangeable soil fraction to less available organic bond fraction. Additionally, they reported that the application of the two feedstock-derived BCs increased the root and shoot dry biomass and decreased the accumulation of Cd, Cu, and Pb in Indian mustard (*Brassica juncea*), thus illustrating the role of biochar in reducing metal phytoavailability while supplying plant nutrients, regardless of the feedstock source. However, according to the authors, the CMB was more effective in metal immobilization and plant growth than the GWB.

A significant decrease in the transfer factor values (TF) of PTMs (Zn, Pb, and Cd) from ryegrass roots to ryegrass shoots when evaluating PLB and SGB additions to a multi-metal contaminated soil was found by [22], and that the PLB was more efficient in such reduction than SGB. This was probably a consequence of their higher pH, CEC, specific surface area (SSA), and stronger buffering capacity as reported by [23], which resulted in the higher efficiency of PLB in decreasing PTMs uptake, as highlighted by the higher decrease of the bioconcentration factor (BCF = [PTMs in shoots/PTMs concentration in soil]) as PLB application rates increased. **Figure 5** (and **Figure 3**) briefly summarizes such findings and highlights the PTMs immobilization as a function of two feedstocks derived-biochar application rates.

When comparing other soil amendments or feedstocks (raw material) with a feedstock-derived biochar, [40] showed that mussel shells, cow manure, and oak wood biochar application reduced Pb phytoavailability and phytoavailability in a highly contaminated military shooting range soil in Korea. Their study also showed increases in germination percentage and root elongation of lettuce (*Lactuca sativa*) in soil treated with the tested amendments, indicating a reduction of Pb accessibility. Outstandingly, biochar was more effective in decreasing Pb availability than the other tested soil amendments [40]. The application of BCs derived from animal wastes (pig manure biochar, and PLB) reduced the mobility of Cu, Cd, Pb and Zn from 28 to 69%, 77 to 100%, 94 to 99%, and 15 to 97%, respectively, in a multi-metal contaminated soil [41].

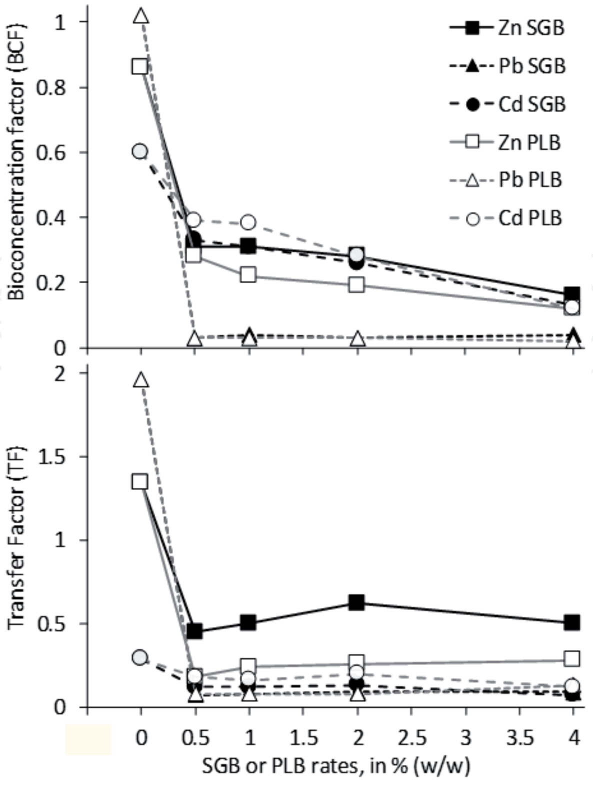

Figure 5.
Bioconcentration factor (BCF) and transfer factor (TF) of potentially toxic metals (Zn, Pb, and Cd) from ryegrass roots to ryegrass shoots as a function of biochar application rates. Biochars were either derived from switchgrass (SGB) or poultry litter (PLB) feedstocks. Graphs were modified from [22].

A study conducted by [42] observed that the addition of hardwood-derived biochar (HWB) to a PTMs contaminated mine soil reduced pore water solubility of Pb concentrations and ryegrass Pb levels. On the other hand, the combination of biochar with greenwaste compost (GWC) was more effective in reducing Pb in soil pore water and uptake by ryegrass. However, the biochar itself was more effective in reducing pore water Cu than GWC. Additionally, [43] reported that the addition of HWB and GWC to a multi-element contaminated soil significantly reduced concentrations of Cd and Zn in pore water during a 60 days exposure to field conditions and reduced phytoavailability of these elements resulting in increased shoot emergence of ryegrass. In contrast, concentrations of Cu and As in pore water increased with amendment applications [38, 43]. In a laboratory column study, [44] reported that HWB reduced the concentrations of Cd and Zn in leachate obtained from a multi-metal polluted soil with evidence of surface retention of both metals on biochar.

The work of [45] compared the impacts of broiler litter-derived biochar and pecan shell-derived steam activated carbon amendments on PTMs (Cu, Ni, and Cd) immobilization and the effects of oxidation on mineral retention in synthetic rainwater leaching experiments. Conversely, their study found that biochar was most effective in immobilizing Cu, whereas activated carbon immobilized Ni and Cd to a larger extent than biochar.

Contrarily, some BCs might only slightly decrease or even significantly increase extractable PTMs depending on the feedstock and pyrolytic temperature [33, 42]. Overall, the influence of biochar on PTMs extractability varies depending on the feedstock, application rate, and BCs particle size [46]. Generally speaking, biochar is a promising tool to reduce the mobility of PTMs in mining areas [22].

4. The effects of biochar conversion processes on PTMs phytoavailability

Biochars are effective in the immobilization of PTMs and this effect varies depending on biochar nature and pyrolysis conditions. [47] investigated the impact of pyrolysis temperature on BCs ability to stabilize PTMs in Small Arms Range soil using broiler litter BCs produced at 350 and 650°C. They found that both BCs were effective in stabilizing Pb and Cu at application rates of $\leq 5\%$ without releasing Sb. In other experiments, [48, 49] suggested using BCs prepared at high temperatures, 650–800°C, for remediation purposes. Additionally, the uptake of PTMs by ryegrass planted in biochar-treated soils generally decreased with increasing pyrolytic temperature [33]. It was also pointed out by [50] that two different feedstocks-derived BCs were more effective in chromium (Cr) adsorption when pyrolyzed at higher temperatures. However, low-temperature biochar was more effective in stabilizing Pb than high-temperature biochar [47]. Such a result was attributed to the higher soluble P concentration of low-temperature biochar, which resulted in a greater Pb immobilization by the formation of lead-phosphate precipitates. In similar experiments using oxidized and unoxidized plant-derived BCs, [49] observed that oxidized BCs rich in carboxyl functional groups had greater ability for Pb, Cu, and Zn immobilization than unoxidized BCs. Therefore, the effect of BCs on the mobility of PTMs in soil is not only a function of the pyrolysis temperature, but also the feedstock used, as previously mentioned, soil properties, and surface functional groups. Indeed, the ability of BCs in reducing the phytoavailability of PTMs in soil depends on its surface functional groups, specific surface area, and porosity [23].

Figure 6 was adapted from the recent work of [51] and clearly shows that simply increasing pyrolysis temperature of BCs to enhance PTMs immobilization is not a pragmatism. The recovery efficiency (RE, in %) of PTMs (in a multi-metal contamination scheme: Pb + Cu + Zn) from soils amended with mesquite BCs (MBC) pyrolyzed at four different temperatures (300, 400, 500, and 600°C), have decreased as the initial concentration of added PTMs increased (**Figure 6**). However, MBC pyrolyzed at the highest temperature (600°C) has shown an overall higher RE% of Pb, Cu, and Zn (**Figure 6**). The authors also emphasized that there was a competitive adsorption among the PTMs into BCs exchangeable sites with a preferable affinity for Pb sorption. That would probably favor other PTMs to be phytoavailable in the medium. According to [22, 23, 51], surface functional groups responsible for metals retention are prone to change when pyrolysis temperature increases, which changes metals' sorption effectiveness to the same extent. Phenolic groups (OH) decrease followed by the increase of aromatic carbon contents (C=C stretching) in produced BCs are attributed to the depolymerization and dehydration of materials as pyrolysis temperature increases, then resulting in the formation of C=C double bonds, carbonyl, and carboxylic functional groups [23, 51, 52, 53]. Those functional groups are also responsible for PTMs adsorption and complexation.

Biomass gasification has also been demonstrated as an alternative method of pyrolysis to produce BCs [54, 55], although to a much lesser extent. It is a

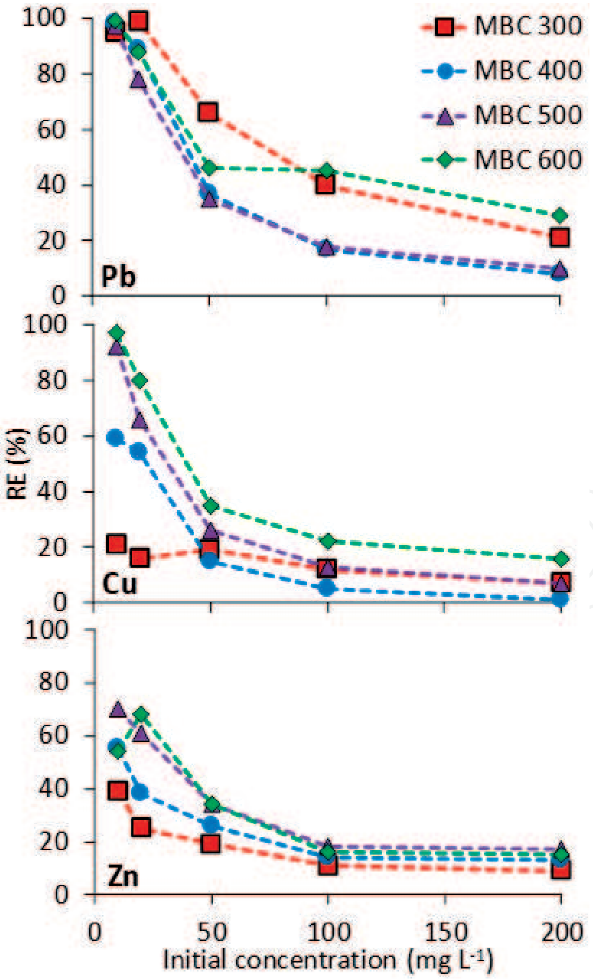

Figure 6.
Lead (Pb), copper (Cu), and zinc (Zn) removal efficiency (RE%) (PTM adsorption) in a multi-metal contaminated soil amended with biochars derived from mesquite and pyrolyzed at 300°C (MBC 300), 400°C (MBC 400), 500°C (MBC 500), and 600°C (MBC 600). The graph is modified from [51] published work.

technology that uses a controlled process involving heat, steam, and oxygen to convert biomass to hydrogen (and other products), in the absence of combustion. A recent study of [55] have demonstrated that the SSA, CEC, and basic functional groups of the pine woodchips-derived BCs (PWC) increased as the rate of airflow increased during the BCs conversion process. Therefore, such improved properties would favor PTMs immobilization in contaminated soils if a proper rate of PWCs were applied. More studies on different gasification processes of applied BCs affecting PTMs mobility in soils are encouraged to broaden the BCs options for remediation purposes.

5. Mechanisms of PTMs adsorption into biochars

The mechanisms proposed for PTMs immobilization are explored in [56, 57]. In summary, three mechanisms are mostly responsible for PTMs retention into BCs, among them: (1) PTMs exchange with calcium (Ca^{2+}), magnesium (Mg^{2+}), and other cations associated with BCs (**Figure 7**); (2) complexation of PTMs into different surface functional groups, as previously highlighted (see Section 4); and (3) the physical adsorption followed by surface precipitation contributing to PTMs immobilization.

In the first case, the PTMs/cations exchange is further attributed to the co-precipitation of PTMs and their innersphere complexation with complex humic matter and mineral oxides contained in the biochar [57]. First, the strengths of PTMs adsorption into BCs surface are low due to the presence of water molecules surrounding the ion (oscillation in the distance of the electrostatic retention). Latterly, water molecules are released and the affinity to complexation enhances depending on the composition and structure of the biochar reactive surface, thus a much stronger inner-sphere complex is formed disfavoring the PTMs release back to the soil solution. In the second case, the PTMs inner-sphere complexation is with the free hydroxyl of mineral oxides surface (OH) and other surface precipitation [57]. In the third case, the surface precipitation of PTMs occurring is designated as *amorphorse*, since biochars present an amorphous although highly reactive structure, similarly as the organic matter compounds [58].

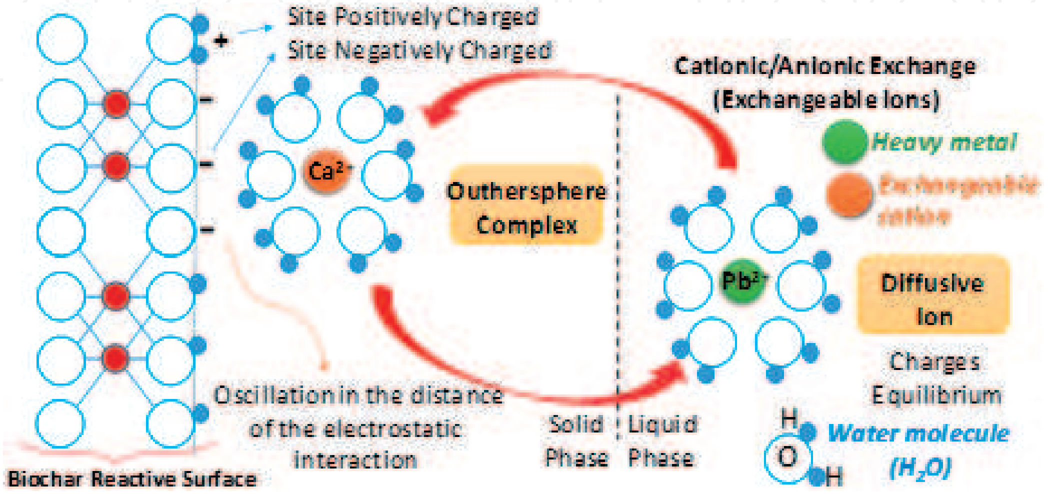

Figure 7.
Mechanisms of cation exchange between positively charged ions contained in the reactive surface of biochars and potentially toxic heavy metals ('heavy metal') dissolved in soil solution. The graph was made by the authors.

6. Conclusions and final considerations

Most studies from the last decade have demonstrated the strong potential of BCs in reducing leachability and immobilizing PTMs pollutants in soils that were previously phytoavailable. By increasing soil pH, BCs act as liming materials and PTMs precipitate as insoluble PTMs hydroxides in a high pH environment. Additionally, the greater SOC attributed to the BCs addition to multi-metal contaminated soil contributes to the formation of PTMS-organic anion complexes that are precipitated out from the system, since the previous bioavailable PTMs contents were much higher than usual. The characteristics of BCs vary widely with different feedstocks (biomass materials) and pyrolysis conditions (low and high temperatures). Generally, there are three mechanisms related to the direct removal of PTMs (and other pollutants) towards BCs reactive surface, which are related to a strong sorption and weak desorption of cationic PTMs then indicating that BCs sequesters pollutants in itself.

The current works emphasizing the use of biochar for soil remediation purposes have mainly been conducted in laboratories and/or greenhouses on a small scale with controlled conditions. As pointed out by [57], large-scale field trials are essential before operational scale remediation projects are implemented. Since the BC properties are largely varying, and sometimes contrasting, it is important to design BC products for every specific remediation project. The BCs ability to sequestrate may lead to the accumulation of PTMs contaminants in the amended soils in the long-term, and yet the pollutant environmental fate over time is not well elucidated. It is well known that the capacity of BCs to adsorb and/or complex PTMs decreases with time as a consequence of the aging process and saturation. Therefore, it is strongly encouraged to research on the aging process of BCs activity in the future because such information would help in the decision-making of the BC application rate and frequency to improve soil PTMs remediation efficiency.

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References

[1] International Biochar Initiative (IBI) (Hg.). Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil [Internet]. Climate Engineering - Kiel Earth Institute. 2012. Available from: https://www.climate-engineering.eu/single/international-biochar-initiative-ibi-hg-2012-standardized-product-definition-and-product-testing-guidelines-for-biochar-that-is-.html [cited 13 March 2020]

[2] Lehmann J, Joseph S. Biochar for Environmental Management: Science, Technology and Implementation. London: New York; 2015

[3] Yuan Y, Bolan N, Prévoteau A, Vithanage M, Biswas JK, Ok YS, et al. Applications of biochar in redox-mediated reactions. Bioresource Technology. 2017;**246**:271-281

[4] Chen B, Zhou D, Zhu L. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. Environmental Science & Technology. 2008;**42**(14):5137-5143

[5] Jang HM, Kan E. Engineered biochar from agricultural waste for removal of tetracycline in water. Bioresource Technology. 2019;**284**:437-447

[6] Li D, Zhao R, Peng X, Ma Z, Zhao Y, Gong T, et al. Biochar-related studies from 1999 to 2018: A bibliometrics-based review. Environmental Science and Pollution Research. 2019;**27**(3):2898-2908

[7] Lehmann J, Gaunt J, Rondon M. Bio-char sequestration in terrestrial ecosystems—A review. Mitigation and Adaptation Strategies for Global Change. 2006;**11**(2):403-427

[8] Lehmann J. Bio-energy in the black. Frontiers in Ecology and the Environment. 2007;**5**(7):381-387

[9] Woolf D, Amonette JE, Street-Perrott FA, Lehmann J, Joseph S. Sustainable biochar to mitigate global climate change. Nature Communications. 2010;**1**(1):1-9

[10] Stevenson FJ. Humus Chemistry: Genesis, Composition, Reactions. New York: John Wiley; 1994

[11] Glaser B, Lehmann J, Zech W. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal—A review. Biology and Fertility of Soils. 2002;**35**(4):219-230

[12] Petter FA, Madari BE, Silva MASD, Carneiro MAC, Carvalho MTDM, Júnior BHM, et al. Soil fertility and upland rice yield after biochar application in the Cerrado. Pesquisa Agropecuária Brasileira. 2012;**47**(5):699-706

[13] Gunten KV, Hubmann M, Ineichen R, Gao Y, Kurt KO, Alessi DS. Biochar-induced changes in metal mobility and uptake by perennial plants in a ferralsol of Brazil's Atlantic forest. Biochar. 2019;**1**(3):309-324

[14] Lehmann J. Amazonian Dark Earths: Origin Properties Management. Dordrecht: Kluwer Academic Publishers; 2003

[15] Ahumada I, Sepúlveda K, Fernández P, Ascar L, Pedraza C, Richter P, et al. Effect of biosolid application to Mollisol Chilean soils on the bioavailability of heavy metals (Cu, Cr, Ni, and Zn) as assessed by bioassays with sunflower (*Helianthus annuus*) and DGT measurements. Journal of Soils and Sediments. 2014;**14**(5):886-896

[16] Chan KY, Zwieten LV, Meszaros I, Downie A, Joseph S. Using poultry litter biochars as soil amendments. Soil Research. 2008;**46**(5):437

[17] Novak JM, Busscher WJ, Laird DL, Ahmedna M, Watts DW, Niandou MAS. Impact of biochar amendment on fertility of a Southeastern coastal plain soil. Soil Science. 2009;**174**(2):105-112

[18] Houben D, Evrard L, Sonnet P. Mobility, bioavailability and pH-dependent leaching of cadmium, zinc and lead in a contaminated soil amended with biochar. Chemosphere. 2013;**92**(11):1450-1457

[19] Streubel JD, Collins HP, Garcia-Perez M, Tarara J, Granatstein D, Kruger C. Influence of contrasting biochar types on five soils at increasing rates of application. Soil Science Society of America Journal. 2011;**75**(4):1402-1413

[20] Peng X, Ye L, Wang C, Zhou H, Sun B. Temperature- and duration-dependent rice straw-derived biochar: Characteristics and its effects on soil properties of an Ultisol in southern China. Soil and Tillage Research. 2011;**112**(2):159-166

[21] Laird D, Fleming P, Wang B, Horton R, Karlen D. Biochar impact on nutrient leaching from a Midwestern agricultural soil. Geoderma. 2010;**158**(3-4):436-442

[22] Antonangelo JA, Zhang H. Heavy metal phytoavailability in a contaminated soil of northeastern Oklahoma as affected by biochar amendment. Environmental Science and Pollution Research. 2019;**26**(32):33582-33593

[23] Antonangelo JA, Zhang H, Sun X, Kumar A. Physicochemical properties and morphology of biochars as affected by feedstock sources and pyrolysis temperatures. Biochar. 2019;**1**(3):325-336

[24] Devi P, Saroha AK. Simultaneous adsorption and dechlorination of pentachlorophenol from effluent by Ni–ZVI magnetic biochar composites synthesized from paper mill sludge. Chemical Engineering Journal. 2015;**271**:195-203

[25] Zhang W, Zheng J, Zheng P, Qiu R. Atrazine immobilization on sludge derived biochar and the interactive influence of coexisting Pb(II) or Cr(VI) ions. Chemosphere. 2015;**134**:438-445

[26] Ahmad I, Maathuis FJ. Cellular and tissue distribution of potassium: Physiological relevance, mechanisms and regulation. Journal of Plant Physiology. 2014;**171**(9):708-714

[27] Wang J, Wang S. Preparation, modification and environmental application of biochar: A review. Journal of Cleaner Production. 2019;**227**:1002-1022

[28] Lu H, Li Z, Fu S, Méndez A, Gascó G, Paz-Ferreiro J. Effect of biochar in cadmium availability and soil biological activity in an anthrosol following acid rain deposition and aging. Water, Air, & Soil Pollution. 2015;**226**(5):1-11

[29] Xu P, Sun C-X, Ye X-Z, Xiao W-D, Zhang Q, Wang Q. The effect of biochar and crop straws on heavy metal bioavailability and plant accumulation in a Cd and Pb polluted soil. Ecotoxicology and Environmental Safety. 2016;**132**:94-100

[30] Zhang R-H, Li Z-G, Liu X-D, Wang B-C, Zhou G-L, Huang X-X, et al. Immobilization and bioavailability of heavy metals in greenhouse soils amended with rice straw-derived biochar. Ecological Engineering. 2017;**98**:183-188

[31] Bolan N, Kunhikrishnan A, Thangarajan R, Kumpiene J, Park J, Makino T, et al. Remediation of heavy metal(loid)s contaminated soils—To mobilize or to immobilize? Journal of Hazardous Materials. 2014;**266**:141-166

[32] Fellet G, Marchiol L, Vedove GD, Peressotti A. Application of biochar on mine tailings: Effects and perspectives for land reclamation. Chemosphere. 2011;**83**(9):1262-1267

[33] Zhang G, Guo X, Zhao Z, He Q, Wang S, Zhu Y, et al. Effects of biochars on the availability of heavy metals to ryegrass in an alkaline contaminated soil. Environmental Pollution. 2016;**218**:513-522

[34] Abdelhafez AA, Abbas MH, Hamed MH. Biochar: A solution for soil Lead (Pb) pollution. In: The 8th International Conference for Development of the Environment in the Arab World; 2016. pp. 22-24

[35] Uchimiya M, Wartelle LH, Klasson KT, Fortier CA, Lima IM. Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil. Journal of Agricultural and Food Chemistry. 2011;**59**(6):2501-2510

[36] Uchimiya M, Chang S, Klasson KT. Screening biochars for heavy metal retention in soil: Role of oxygen functional groups. Journal of Hazardous Materials. 2011;**190**(1-3):432-441

[37] Uchimiya M, Klasson KT, Wartelle LH, Lima IM. Influence of soil properties on heavy metal sequestration by biochar amendment: 1. Copper sorption isotherms and the release of cations. Chemosphere. 2011;**82**(10):1431-1437

[38] Abdelhafez AA, Li J, Abbas MH. Feasibility of biochar manufactured from organic wastes on the stabilization of heavy metals in a metal smelter contaminated soil. Chemosphere. 2014;**117**:66-71

[39] Park JH, Choppala GK, Bolan NS, Chung JW, Chuasavathi T. Biochar reduces the bioavailability and phytotoxicity of heavy metals. Plant and Soil. 2011;**348**(1-2):439-451

[40] Ahmad M, Lee SS, Yang JE, Ro H-M, Lee YH, Ok YS. Effects of soil dilution and amendments (mussel shell, cow bone, and biochar) on Pb availability and phytotoxicity in military shooting range soil. Ecotoxicology and Environmental Safety. 2012;**79**:225-231

[41] Gondek K, Mierzwa-Hersztek M. Effect of low-temperature biochar derived from pig manure and poultry litter on mobile and organic matter-bound forms of Cu, Cd, Pb and Zn in sandy soil. Soil Use and Management. 2016;**32**(3):357-367

[42] Karami N, Clemente R, Moreno-Jiménez E, Lepp NW, Beesley L. Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass. Journal of Hazardous Materials. 2011;**191**(1-3):41-48

[43] Beesley L, Moreno-Jiménez E, Gomez-Eyles JL. Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. Environmental Pollution. 2010;**158**(6):2282-2287

[44] Beesley L, Marmiroli M. The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar. Environmental Pollution. 2011;**159**(2):474-480

[45] Uchimiya M, Lima IM, Klasson KT, Chang S, Wartelle LH, Rodgers JE. Immobilization of heavy metal ions (CuII, CdII, NiII, and PbII) by broiler litter-derived biochars in water and

soil. Journal of Agricultural and Food Chemistry. 2010;**58**(9):5538-5544

[46] Yang X, Liu J, Mcgrouther K, Huang H, Lu K, Guo X, et al. Effect of biochar on the extractability of heavy metals (Cd, Cu, Pb, and Zn) and enzyme activity in soil. Environmental Science and Pollution Research. 2015;**23**(2):974-984

[47] Uchimiya M, Bannon DI, Wartelle LH. Retention of heavy metals by carboxyl functional groups of biochars in small arms range soil. Journal of Agricultural and Food Chemistry. 2012;**60**(7):1798-1809

[48] Uchimiya M, Klasson KT, Wartelle LH, Lima IM. Influence of soil properties on heavy metal sequestration by biochar amendment: 2. Copper desorption isotherms. Chemosphere. 2011;**82**(10):1438-1447

[49] Uchimiya M, Bannon DI, Wartelle LH, Lima IM, Klasson KT. Lead retention by broiler litter biochars in small arms range soil: Impact of pyrolysis temperature. Journal of Agricultural and Food Chemistry. 2012;**60**(20):5035-5044

[50] Rafique MI, Usman ARA, Ahmad M, Sallam A, Al-Wabel MI. In situ immobilization of Cr and its availability to maize plants in tannery waste-contaminated soil: Effects of biochar feedstock and pyrolysis temperature. Journal of Soils and Sediments. 2019;**20**(1):330-339

[51] Abdin Y, Usman A, Ok YS, Tsang YF, Al-Wabel M. Competitive sorption and availability of coexisting heavy metals in mining-contaminated soil: Contrasting effects of mesquite and fishbone biochars. Environmental Research. 2020;**181**:108846

[52] Bavariani MZ, Ronaghi A, Ghasemi R. Influence of pyrolysis temperatures on FTIR analysis, nutrient bioavailability, and agricultural use of poultry manure biochars. Communications in Soil Science and Plant Analysis. 2019;**50**(4):402-411

[53] Lange J-P. Lignocellulose conversion: An introduction to chemistry, process and economics. Biofuels Bioproduct Biorefining. 2007;**1**(1):39-48

[54] Rivas AMJ, Yuan W, Boyette MD, Wang D. Airflow and insulation effects on simultaneous syngas and biochar production in a top-lit updraft biomass gasifier. Renewable Energy. 2018;**117**:116-124

[55] Rivas AMJ, Yuan W, Wang D, Wang D, Kumar A. The effect of gasification conditions on the surface properties of biochar produced in a top-lit updraft gasifier. Applied Sciences. 2020;**10**(2):688

[56] Lu H, Zhang W, Yang Y, Huang X, Wang S, Qiu R. Relative distribution of Pb2 sorption mechanisms by sludge-derived biochar. Water Research. 2012;**46**(3):854-862

[57] Zhang X, Wang H, He L, Lu K, Sarmah A, Li J, et al. Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. Environmental Science and Pollution Research. 2013;**20**(12):8472-8483

[58] Uchimiya M, Lima IM, Klasson KT, Wartelle LH. Contaminant immobilization and nutrient release by biochar soil amendment: Roles of natural organic matter. Chemosphere. 2010;**80**(8):935-940