



# Using Industrial Sewage Sludge-Derived Biochar to Immobilize Selected Heavy Metals in a Contaminated Calcareous Soil

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## Abstract

Many studies have indicated the effect of biochar on the fractionation of heavy metals in acidic soils, while little information is available on their effects on contaminated calcareous soils. Applying biochar products from sewage sludge pyrolysis as soil amendment was investigated in this study with special attention paid to fractionation of Pb and Cd in calcareous soil around a lead–zinc mine when pyrolysis temperature and biochar application rates were changed. The biochar feedstock was industrial sewage sludge, collected from the Baharan industrial park, using an anaerobic–anoxic–aerobic treatment process at two different temperatures (300 and 600 °C), and then adopted as amendment for the soil. The results revealed that with increasing pyrolysis temperature, the biochar's levels of N, H and O decreased, while its amount of C increased significantly. The highest rate of the biochar application (8%) had lower pH compared to the control soil for both biochars. The soil EC with 8% biochar 300 °C was less than biochar 600 °C, perhaps due to the higher amount of ash in the biochar produced at 600 °C. The results showed that biochar 600 was more porous than biochar 300. The exposed porous structure made the pores more accessible for the adsorbate particles. Therefore, the biochar produced at 600 °C, more effectively, reduced the exchangeable form of Pb and Cd. The organic forms of Pb and Cd increased with increasing levels of biochar application, and this trend was higher in the treated soil with biochar produced at 600 °C due to high organic carbon content. The results showed that most of Pb and Cd existed in the residual form after application of biochar, especially at 600 °C, resulting in a significant reduction in their bioavailability.

**Keywords** Biochar · Fractionation · Cadmium · Zinc · Immobilization · Amendment

## Statement of Novelty

Very few investigations are available to have studied:

- Immobilization of selected heavy metals in a contaminated calcareous soil.
- Effects of biochar produced from industrial sewage sludge at two temperatures on the metals fractionation.
- Industrial sewage sludge-derived biochar immobilized selected heavy metals in a contaminated calcareous soil.

## Introduction

Heavy metal contaminations in soil originate from various sources mainly natural and anthropogenic, including sewage sludge and industrial and mining facilities [1–3]. Toxic and non-degradable nature of heavy metals can lead to irreparable risks to human health, soil quality and environmental systems [4–6]. For instance, the disposal and use of sewage sludge, such as sludge storage or incineration as well as its direct use in agriculture, is known as an important source of soil contamination by heavy metals. Therefore, the development of an acceptable environmental and economic method for sustainable management of sewage sludge is a major environmental concern [7].

The conversion of sewage sludge to biochar can be a potential way to its disposal and an economical and effective alternative for removing pathogens, pollutants and hazardous compounds present in sludge [8, 9]. Biochar is a carbon-rich by-product that is produced by the pyrolysis process of

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biomass under oxygen-limited conditions. Desirable properties of biochar including its surface area, porosity, variety of functional groups and potential for adsorption of organic pollutants and heavy metals have contributed to its potential in controlling the environmental pollutants [7, 10].

O'Connor et al. [3] working on biochar's effectiveness in reducing the impacts of pollution list the followings as important factors: application time and period; some site-specific factors such as climate, biochar dosage rate, and mixing depth; and finally biochar feedstock type, and its properties.

The physical and chemical properties of biochar are mainly influenced by the characteristics of the feedstock source and the pyrolysis conditions. Among the conditions of pyrolysis, the temperature is an important factor of biochar production [11–13]. The temperature of the pyrolysis process greatly affects the surface area and porosity of the biochar. Chen et al. [14] reported that with increasing temperatures from 500 to 900 °C, the porosities and specific surface area increased from 0.056 to 0.099 cm<sup>3</sup>/g and 25.4 to 67.6 cm<sup>2</sup>/g; respectively. Zama et al. [15] also reported that an increase in pyrolysis temperature from 350 to 650 °C resulted in a significant surge in the specific surface areas and porosity of the biochar.

In addition, the pyrolysis temperature could affect the chemistry of the biochar. The amount of heat applied controls the degree of carbonization. Carbonization is the term for the conversion of an organic substance into carbon or a carbon-containing residue through pyrolysis. The increase in carbon content with temperature is due to increasing the degree of carbonization [16, 17]. This decline in oxygen and hydrogen content with temperature happens as a result of carbonization and due to breaking of weaker bonds in biochar structure [18]. Singh et al. [19] observed the lowest and highest O/C ratios of the biochars at 500 and 250 °C, correspondingly. The pyrolysis temperature showed a significant positive correlation with pH values, microporous structure, surface area, fixed C, and ash content; however revealed a negative relationship with yield, average pore size, functional groups, volatile matter, O and H mass fractions, and the number and density of functional groups [20].

Depending on the type of the biochar and the heavy metal, increasing the amount of biochar could significantly reduce the availability of heavy metals. A large number of the pot and field studies on biochar under acidic soil conditions have been conducted due to alkaline nature of biochar produced at high pyrolysis temperature. However, the scenario is quite different in the case of calcareous soil in nature. Although many research exist studying the effects of biochar on the mobility and availability of heavy metals. Nonetheless, little attention has been paid to the role of biochar produced from industrial sewage sludge to improve heavy metals in simulated situ immobilization in contaminated calcareous

soils. However, the effect of the biochar on the fractionation of selected heavy metals has not been fully explained. The aims of this work were: (1) discovering the application levels of the biochar produced from sewage sludge at two different temperatures (300 and 600 °C); (2) determining the effects of biochar produced from sewage sludge at the same situation on electrical conductivity (EC), and pH, as well as (3) and exploring the fractionation of selected heavy metals in a soil around a lead–zinc mine.

## Materials and Methods

### The Biochar and Soil Preparation

Soil samples were collected from the area surrounding the old Ahangaran lead–zinc mine, Iran, which is located 20 km ESE of Malayer in West Central Iran (34°10'N, 48°59'E). The soil was sampled from the top 0–25 cm layer after removing any surface vegetation and litter. The soil samples were then air dried in trays at room temperature (25 °C) for 1 day, ground, and sieved through a 2-mm nylon sieve.

The soil pH and electrical conductivity (EC) were measured using 1:5 soil/water suspensions; whereas total Pb and Cd concentrations were determined by the method of Spósito et al. [21]. The cation exchange capacity (CEC) was analyzed by the method of Bower [22].

The biochar feedstock was industrial sewage sludge, collected from the Baharan industrial park, using an anaerobic–anoxic–aerobic treatment process. First, the sewage sludge sample was air-dried, ground into 2 mm fine particles, stirred and then ground again in a mortar to ensure that the sample was homogenous. Finally, the sewage sludge particles were pyrolyzed with a horizontal quartz reactor at 300 and 600 °C under a flow of N<sub>2</sub> of 1000 mL min<sup>-1</sup>. The BC300 and BC600 represented the sewage sludge biochar produced at the 300 and 600 °C temperatures, respectively. The pyrolysis heating rate was employed at 25 °C min<sup>-1</sup>. The temperature was measured with a thermocouple and held for 3 h. Some physical and chemical properties of the soil and biochars are presented in Table 1.

### Characterization of the Biochars

Biochar was soaked with deionized water at a 1:20 (w/v) solid/water ratio for 1 h. The slurry was then measured for pH and electrical conductivity (EC) using a pH electrode and a conductivity meter; correspondingly. The CEC of the biochars were determined according to procedures described by Bower [22]. Elemental composition (CHNSO) was determined by dry combustion using a CHNS elemental analyzer. The O content was calculated by  $O(\%w/w) = 100 - \text{ash}(\%w/w) - C(\%w/w) - H(\%w/w) - N(\%w/w)$  [23]. Ash content

**Table 1** Some physical and chemical properties of the soil and biochars used in the study

Characteristics	
Textural class	Clay loam
Soil	
Sand (%)	33.2
Silt (%)	36
Clay (%)	30.8
CEC (Cmol(+) Kg <sup>-1</sup> )	29.3
pH	8.2
Organic matter (%)	0.82
EC (dS m <sup>-1</sup> )	0.23
Pb (mg kg <sup>-1</sup> )	7937
Cd (mg kg <sup>-1</sup> )	9.92
BC300	
pH	7.6
EC (dS m <sup>-1</sup> )	3.17
CEC (Cmol(+) kg <sup>-1</sup> )	26.4
Organic matter (%)	32
Ash (%)	45.8
Na (%)	0.23
K (%)	0.56
Ca (%)	0.8
BC600	
pH	8.5
EC (dS m <sup>-1</sup> )	4.15
CEC (Cmol(+) kg <sup>-1</sup> )	31.6
Organic matter (%)	38
Ash (%)	58.2
Na (%)	0.38
K (%)	0.7
Ca (%)	0.93

of the biochar samples was estimated following the ASTM D 3176 standard method by combustion of dry samples at 760 °C for 6 h, and then measured as the residue remained after heating. The ash content was determined according to the following formulae [23]:

$$\text{Ash content [\%]} = \frac{\text{weight of ash}}{\text{dry weight of biochar}} \times 100$$

### Analysis of the Biochar Micromorphology Using the Scanning Electron Microscope

A scanning electron microscope (SEM) was utilized to assess the micromorphology of both the biochars. Prior to being scanned by an electron microscope model (JSM-810A, JEOL, Japan), each biochar sample was coated with a thin layer of gold and mounted on a copper slab using a double-stick carbon tape.

### Characterization of the Surface Functional Groups Using the FTIR Spectroscopy

For characterizing the surface functional groups on the biochar, the Fourier Transformation Infrared Spectroscopy (FTIR) was employed. Approximately 1 mg of the finely ground biochar was gently mixed with 200 mg of oven-dried (105–110 °C) KBr. The mixture was then pressed into a pellet for FTIR analysis. The FTIR spectrum of biochars, with and without Pb and Cd adsorbed, was recorded using a Perkin Elmer spectrum 65 scanning from 4000 to 500 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>.

### The Laboratory Incubation Experiment

Treatments consisted of the addition of 0, 2, 4 and 8% (w/w) of the biochars, produced from industrial sewage sludge at the 300 and 600 °C temperatures, to the soil. For each test, three replicate containers were used, each containing approximately 500 g of the soil (dry weight equivalent). The test containers were covered with perforated lids to limit water loss due to evaporation, and then kept in a climate chamber (16 h light, 8 h dark at 23 ± 2 °C, relative humidity of 75 ± 5%) for 42 days. The method of Rey et al. [24] was followed to examine the soil water holding capacity. In brief, 100 g of soil was placed in a metal cylinder and the bottom was covered with plastic net to prevent any soil losses, before soaking in tap water for 24 h to saturate the soil. The soil was covered with a plastic sheet to prevent evaporation, and then left for 72 h to drain before weighing. The soil was oven-dried to constant mass at 105 °C and the retained gravimetric moisture content in the soil was treated as the soil water holding capacity (%). The fractionation of Pb and Cd were conducted according to the scheme proposed by Sposito et al. [21] The chemical extractants employed and the extraction periods were as the followings: KNO<sub>3</sub> 0.5 mol dm<sup>-3</sup> (25 mL extractant shaken for 16 h), NaOH 0.5 mol dm<sup>-3</sup> (residue from step 1 shaken for 16 h with 25 mL extractant), Na<sub>2</sub>EDTA 0.05 mol dm<sup>-3</sup> (residue from step 2 shaken for 6 h with 25 mL extractant), and HNO<sub>3</sub> 4 mol dm<sup>-3</sup> (residue from step 3 heated for 16 h at 80 °C with 25 mL extractant). The Pb and Cd concentrations in the extracts were determined by flame atomic absorption spectrophotometry (Varian AA-220). The fractions were designated (in order given above) as the exchangeable, bound to organic matter, bound to carbonates, and residual fractions.

### Statistical Analysis

Statistical analysis of the data was performed using a SPSS 16.0 statistical package program (SPSS Inc., USA). One-Way ANOVA was applied to test the data and the Duncan's multiple range tests ( $p \leq 0.05$ ) was used to detect the

statistical significance of the treatments on soil pH, EC and fractionation of Pb and Cd.

## Results and Discussion

### Elemental Analysis of the Biochars Produced from Industrial Sewage Sludge

The results of the elemental analysis showed with increasing pyrolysis temperature, the biochar's levels of N, H and O decreased, while its amount of C increased significantly. Consequently, the biochar's proportion of hydrogen and oxygen over carbon also reduced gradually (Table 2). Wu et al. [10] found similar results while working on biochar either from raw straw or peanut shells and coconut coir, respectively. Zhao et al. [20] reported that the C content increased from 47.5 to 80.2%; while H and O contents decreased from 5.9 to 1.3% and from 39.5 to 5.3%; respectively, as the pyrolysis temperature increased from 200 to 700 °C. According to Kim et al. [11], the gradual reduction of hydrogen-carbon and oxygen-carbon ratios happen due to eventual construction of condensed C. It was confirmed by the FTIR data too. It was observed that functional groups of the hydroxyl (–OH; 3600–3200  $\text{cm}^{-1}$ ), alkene (1660–1580  $\text{cm}^{-1}$ ), and symmetric C–O stretching (1200–1000  $\text{cm}^{-1}$ ) lessened when the pyrolysis temperature increased (see below the FTIR results).

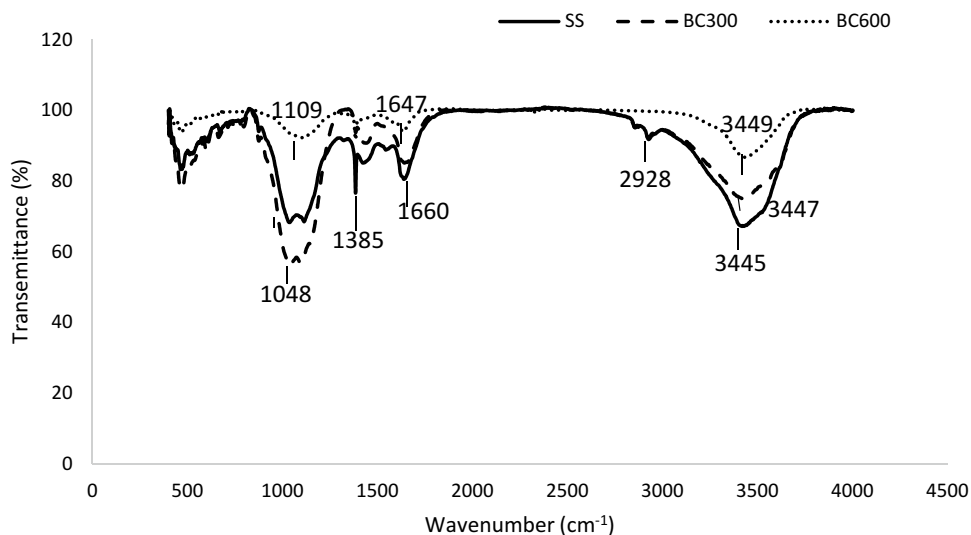
### The Functional Groups Analysis

The FTIR spectrums of the sewage sludge (SS) and its biochars are compared in Fig. 1. A large number of functional groups were shown on the surfaces of the biochars, which could be beneficial for sorption. With increasing the pyrolysis temperature, the functional groups' peaks and intensity decreased on both the sewage sludge and the biochar including the peak intensity of H bonded O–H groups of phenols, alcohols, organic acids, and N–H as well as the hydroxyl groups (3600–3200  $\text{cm}^{-1}$ ), aliphatic  $\text{CH}_3$  asymmetric (2925  $\text{cm}^{-1}$ ), alkene C=C stretching vibration (1660–1580  $\text{cm}^{-1}$ ), carboxyl-carbonate structure, aromatic C=C bond, the aromatic ring's various substitution modes (1400–1380), and symmetric C–O stretching (1200–1000  $\text{cm}^{-1}$ ) [25, 26]. The sharp peak at 3445 in the SS, and the weak peaks at around 3447 and 3449  $\text{cm}^{-1}$  in BC300 and BC600 observed as a result of the phenol's functional group and stretching of the hydroxyl group (–OH) (Fig. 1). Zhang et al. [27] reported that the wide peak seen at 3400  $\text{cm}^{-1}$  was due to the hydroxyl (–OH) stretching, while sharp reduction of the peak intensity at samples 300–500 °C were seen as a result of an eruptive loss of –OH. The peaks at 2928  $\text{cm}^{-1}$  seen in the SS and BC300 are assigned to aliphatic C–H deforming vibration. These functional groups disappeared at the 600 °C temperature (Fig. 1). The peak at 2925  $\text{cm}^{-1}$  corresponds to the aliphatic  $\text{CH}_3$  asymmetric stretching vibration depending on the amount

**Table 2** The elemental analysis of the biochar produced from sewage sludge

Treatment	Component (%)				Atomic ratio	
	N	C	H	O	H/C	O/C
BC300	9.42	18.06	2.28	24.4	1.511	1.01
BC600	3.38	28.94	1.90	7.58	0.78	0.19

**Fig. 1** FTIR analysis results of the biochars produced from sewage sludge



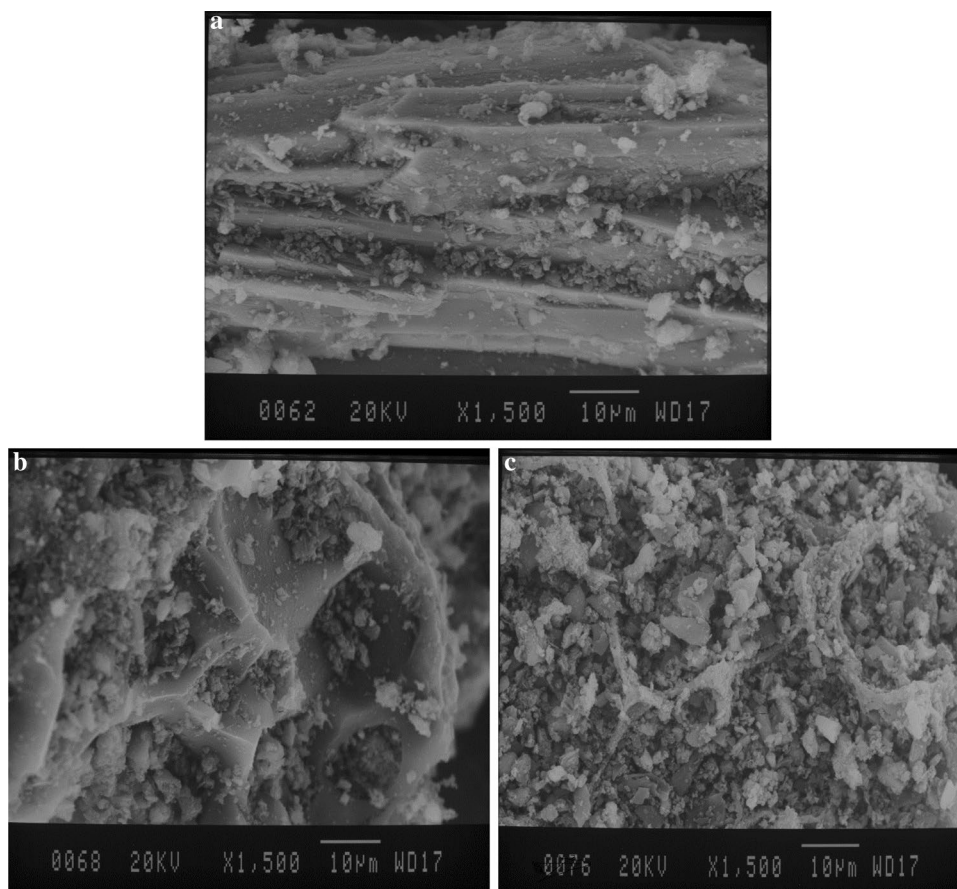
of sewage sludge fats and lipids [27]. Constant reduction of the labile aliphatic compounds as accompanied by the demethylation and dehydration could be blamed for reduction of the peak intensities. The reduction of  $-OH$  and aliphatic groups besides a simultaneous increase of fused-ring structures boosted the pore formation [26]. Singh et al. [19] similarly reported that with increased pyrolysis temperature the functional groups decreased while the condensed C increased. Similar results were obtained in some other studies, for instance: an increase in pyrolysis temperature resulted in a decrease in  $O-H$  stretching at  $3500-3200\text{ cm}^{-1}$  attributable to hydrogen bonded hydroxyl groups; while the asymmetric ( $2935\text{ cm}^{-1}$ ) and symmetric ( $2885\text{ cm}^{-1}$ )  $C-H$  stretchings for aliphatic functional groups decreased [16, 28]. The sharp peak at  $1660$  in the SS and BC300, and the pore peaks at  $1647\text{ cm}^{-1}$  in BC600 corresponded to the alkene  $C=C$  stretching vibration. A peak is observed around the  $1385\text{ cm}^{-1}$  in SS (Fig. 1). Moreno-Castilla et al. [29] reported that the bands in the range of  $1400-1380\text{ cm}^{-1}$  can be attributed either to a carboxyl-carbonate structure, an aromatic  $C=C$  bond, or various substitution modes of the aromatic ring. The functional groups' peak intensity of the symmetric  $C-O$  stretching ( $1200-1000\text{ cm}^{-1}$ ) decreased with increasing the pyrolysis temperature (in the BC600) (Fig. 1).

We believe that the biochar produced at higher temperature was more stable. The lower atomic hydrogen-carbon proportion, calculated for the BC600 (Table 2) could be as a result of having higher amount of the aromatic carbon compounds. This finding is supported by the FTIR spectra of the biochars (Fig. 1). Singh et al. [19] showed that biochars pyrolyzed at higher temperature had more stable C skeleton. We could also confirm findings by Nguyen et al. [30] who revealed the aromaticity of the biochar could increase as a result of higher pyrolysis temperature.

### Surface Morphology SEM

The SEM micrographs of the sewage sludge, the BC300 and the BC600 are illustrated in Fig. 2a-c; in that order. The sewage sludge was more inerratic and flat, while biochars produced at 300 and 600 °C had several cracks and holes on its surface. Jin et al. [31] reported that with increasing the pyrolysis temperature, the surface morphology and porous structure of biochars progressively developed. Moreover, when the pyrolysis temperature increased, the changes in texture continued. It was revealed by the rougher and more porous surface on which some highly conjugated aromatic compounds were found [32]. Enhanced biomass

**Fig. 2** a the SEM picture of the sewage sludge. b the SEM picture of the biochar at 300 °C. c the SEM picture of the biochar at 600°C





decomposition due to higher temperature and more severe pyrolysis could be mentioned as the reasons behind it. Based on the outward appearance, it could be said that the pores are not cross-linked. The biochar produced at 300 °C remained more porous on its surface. When the temperature increased to 600 °C, there appeared to be more microporous but the biochar surface was less rough. Zhang et al. [26] reported that subtle volatilization at higher temperature led to more pore and void creation in the biochar. Furthermore, when chemical bonds break and complexes melt, more pores are created in the structure of the material [33].

### Effects of the Biochar on the Soil Organic Carbon

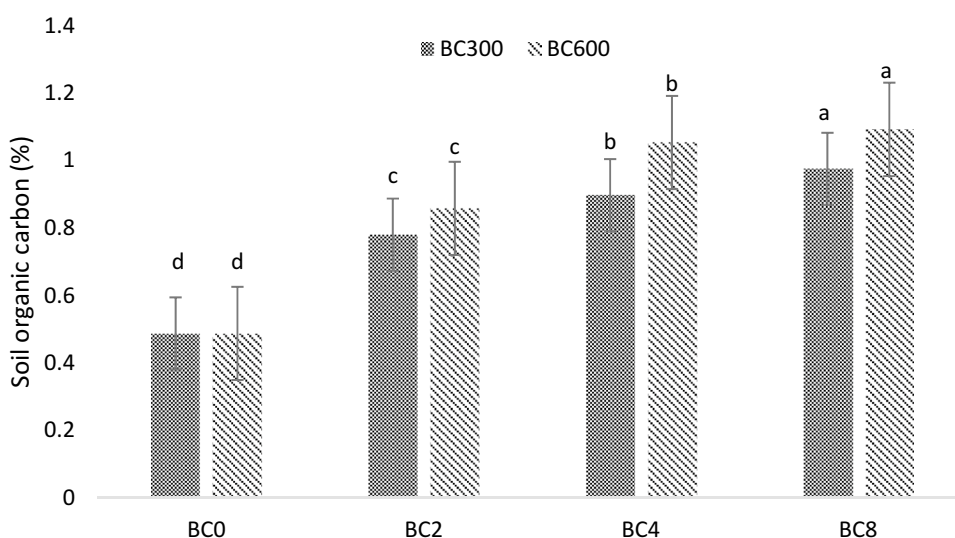
The application of different rates of biochar produced at the temperatures of 300 and 600 °C had significant effect on soil organic carbon (Table 3). Shenbagavalli and Mahimairaja [34] showed that applying different amounts of biochar significantly affected the content of soil organic carbon. With the application of biochar at the rate of 8%, the soil organic carbon increased from 0.49 to 0.98 and 1.09% at BC300 and BC600; respectively. The trend of increasing organic carbon in the soil treated with biochar produced at the temperature of 600 °C was higher than that of the soil treated with biochar produced at the temperature of 300 °C (Fig. 3).

**Table 3** Effects of the biochar application rate produced at the temperatures of 300 and 600 °C on the soil organic carbon

Source of variation	df	BC300		BC600	
		MS	P	MS	P
Biochar application rate (BC)	3	0.137	0.000	0.229	0.000
Error	8	0.000		0.000	

*df* degrees of freedom, *MS* mean square

**Fig. 3** Effect of the biochar application rate produced at the temperatures of 300 and 600 °C on the soil pH under controlled laboratory conditions. (BC<sub>0</sub> = no biochar added as control; BC<sub>2</sub> = applied 2% biochar; BC<sub>4</sub> = applied 4% biochar; BC<sub>8</sub> = applied 8% biochar). Bars that do not share a common letter represent values that are significantly different at  $P \leq 0.05$



As biochar is an organic carbonaceous material, the treatment of polluted land with biochar will inherently increase the organic carbon content of the soil. As such, the greater the biochar dosage rate, the greater would be the increase in organic carbon [3].

### Effects of the Biochar on the Soil pH

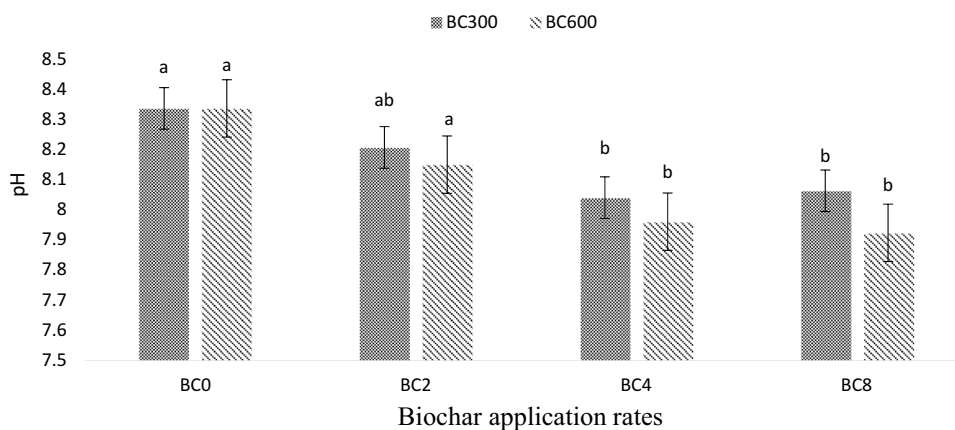
The analysis of data showed that biochar application level had significant effect on soil pH (Table 4). As the pyrolysis temperature was increasing, the soil pH decreased. Increase in the application rate of the biochar decreased the soil pH right from its start. With the application of biochar at the rate of 8%, the soil pH reduced from 8.34 to 8.06 and 7.92 at BC300 and BC600; respectively (Fig. 4). Few studies demonstrate a reduction of pH due to an addition of biochar into alkaline soils [34]; however, some evidence suggests that the acid biochar's addition to the acidic soils could reduce the soil pH [35]. However, Liu and Zhang [36] revealed that instead of raising the pH, the addition of biochar to alkaline soils, only created a declining pH trend. The pH of the calcareous soil used in this study was 8.2 (Table 1), likely prohibiting the biochar liming effect. Meanwhile, biochar could increase the oxidation of organic matter in soil, producing acidic matter

**Table 4** Effects of the biochar application rate produced at the temperatures of 300 and 600 °C on the soil pH

Source of variation	df	BC300		BC600	
		MS	P	MS	P
Biochar application rate (BC)	3	0.057	0.043	0.067	0.013
Error	8	0.013		0.010	

*df* degrees of freedom, *P* probability level, *MS* mean square

**Fig. 4** Effect of the biochar application rate produced at the temperatures of 300 and 600 °C on the soil pH under controlled laboratory conditions. (BC<sub>0</sub>=no biochar added as control; BC<sub>2</sub>=applied 2% biochar; BC<sub>4</sub>=applied 4% biochar; BC<sub>8</sub>=applied 8% biochar). Bars that do not share a common letter represent values that are significantly different at  $P \leq 0.05$



[37, 38]. The construction of the acidic functional groups can nullify alkalinity and eventually decline soil pH [36]. Soil treated with BC600 had a higher carbon content compared to soil treated with BC300 (Fig. 3). The oxidation and decomposition of soil organic matter coming from high organic carbon content leads significantly decrease the soil pH [36].

Van Zwieten [37] reported that the biochar application, with either pH value of 9.4 or 8.2, increased the pH of Ferrosol (initial pH at 4.2), but only the later increased the pH value of Calcarosol (initial pH was at 7.67). Addition of biochar into a mine tailing soil increased the pH from 8.13 into 10.2 [38]. These results are contrary to our results, which showed that the application of biochars led to a reduction of the soil pH.

Carbonates and soluble base cations make a biochar composition including calcium and magnesium [37, 39]. The biochar cation content could be behind the decline in pH. Slightly soluble carbonates are created by combining cations and the carbonates in the soil. It later constrains the carbonates’ hydrolyzation, leading to decreased hydroxyl content. Thus, the addition of the biochar reduced the soil pH to some extent [36].

**Effect of the Biochar on the Soil EC**

The results revealed that the biochar application rate had significant effects on soil EC (Table 5). The soil EC increased with enhancing the pyrolysis temperature, so that the soil EC was lower at the BC300 compared to the BC600. The highest rate of the biochar application (8%) had significantly higher EC, compared to the control (Fig. 5). The increase in EC can likely be attributed to high amount of ash in the biochars. Previous studies also show that biochar contains some elements such as K, Ca, and Mg and when applied to soil, it could increase its EC [39, 40].

**Table 5** Effects of the biochar application rate produced at the temperatures of 300 and 600 °C on the soil EC

Source of variation	df	BC300		BC600	
		MS	P	MS	P
Biochar application rate (BC)	3	0.069	0.001	0.177	0.000
Error	8	0.004		0.002	

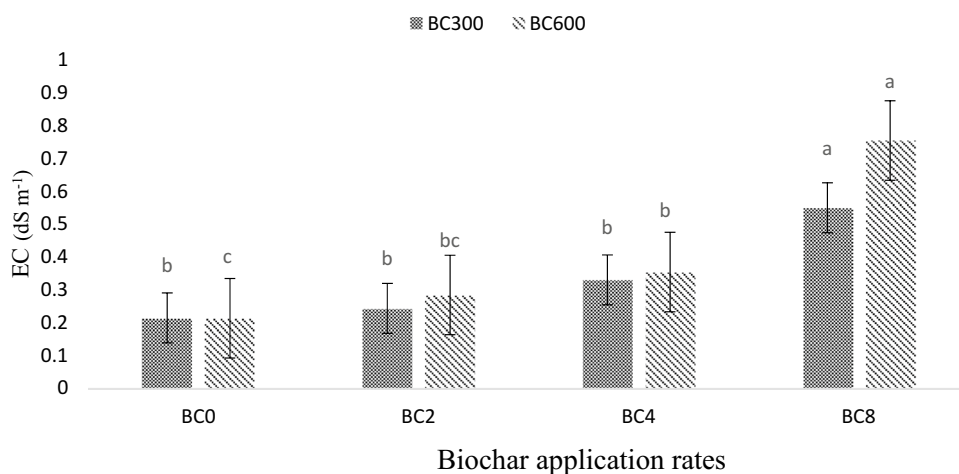
df degrees of freedom, P probability level, MS mean square

**Effect of the Biochar on the Fractionation of Pb and Cd in the Soil**

In this work, the sequential extraction method proposed by Sposito et al. [21] was employed to examine whether the two biochars, produced at the temperatures of 300 and 600 °C, could affect fractional distribution of heavy metals in the soils. The treated soil samples were exposed to the sequential extraction, in which heavy metals were allocated into the exchangeable (EXC), the bound to carbonates (CAR), the bound to organic matter (ORG) and the residual (RES).

The sequential extraction results for Pb in the soil are shown in Table 6. The distributions of different forms of Pb were significantly affected by the pyrolysis temperature. Increased pyrolysis temperature and biochar application rate significantly decreased the concentration of Pb in the exchangeable and carbonate forms. The results showed that the organic and residual forms of the metals increased after the biochar application (Fig. 5). The application of biochar can change soil chemical properties such as pH, EC and organic carbon and then modify the existing fractionation of soil heavy metals [41]. The adsorption property of biochar could affect the migration, transformation, and biological toxicity of the soil [16]. “Biochar can increase the contents of soil organic matters and soil CEC and then increase complexation of soil heavy metal ions, so it can also decrease the contents of exchangeable heavy metal”[42]. Cao et al. [43] found that biochar could induce

**Fig. 5** Effect of the pyrolysis temperature and biochar application rate on the soil EC under controlled laboratory conditions (BC<sub>0</sub>=no biochar added as control; BC<sub>2</sub>=applied 2% biochar; BC<sub>4</sub>=applied 4% biochar; BC<sub>8</sub>=applied 8% biochar). Bars that do not share a common letter represent values that are significantly different at  $P \leq 0.05$



**Table 6** Effect of the biochar application rate produced at the temperatures of 300 and 600 °C on the fractionation of Pb

Extractable Pb fractions	Sources of variation	df	BC300		BC600	
			MS	P	MS	P
EXC	Biochar application rate (BC)	3	0.406	0.013	0.469	0.000
	Error	8	0.059		0.038	
ORG	Biochar application rate (BC)	3	1713.574	0.000	3272.168	0.000
	Error	8	12.402		14.355	
CAR	Biochar application rate (BC)	3	434245.65	0.000	500046.38	0.000
	Error	8	856.934		5954.590	
RES	Biochar application rate (BC)	3	41,240,000	0.000	50,710,000	0.000
	Error	8	43029.785		41408.69	

df degrees of freedom, P probability level, MS mean square

Pb to form  $Pb_3(CO_3)_2(OH)_2$  and  $\beta-Pb_9(PO_4)_6$  precipitations under conditions that are rich in phosphates and carbonates; respectively. The results showed that increasing the biochar pyrolysis temperature reduced the concentration of Pb in the exchangeable forms. The minimum exchangeable fraction of Pb was  $5.7 \text{ mg kg}^{-1}$  for BCs produced at 600 °C which is lower than that of BCs produced at 300 °C ( $7.9 \text{ mg kg}^{-1}$ ) in treatment BC<sub>8</sub> (Fig. 5). Ahmad et al. [44] illustrated that biochars pyrolyzed at higher temperature (i.e., 700 °C) more effectively reduced the Pb bioavailability (Fig. 6).

The sequential analysis of Cd in the soil, treated with the biochar, showed a wide variation of the Cd-forms depending on the pyrolysis temperature (Table 7). The exchangeable and carbonate forms of the Cd were lower in the BC600 amended soil compared to the BC300 one. However, effect of the biochar dosage on different forms of Cd was significant. Increasing the rates of biochar applications significantly reduced the concentration of Cd in the exchangeable and carbonate forms, while organic and residual forms increased (Fig. 7). Fellet et al. [38] utilized the biochar as a remediation of a multi-contaminated mine soil. The addition of the biochar did not bring about the shrinkage of the total

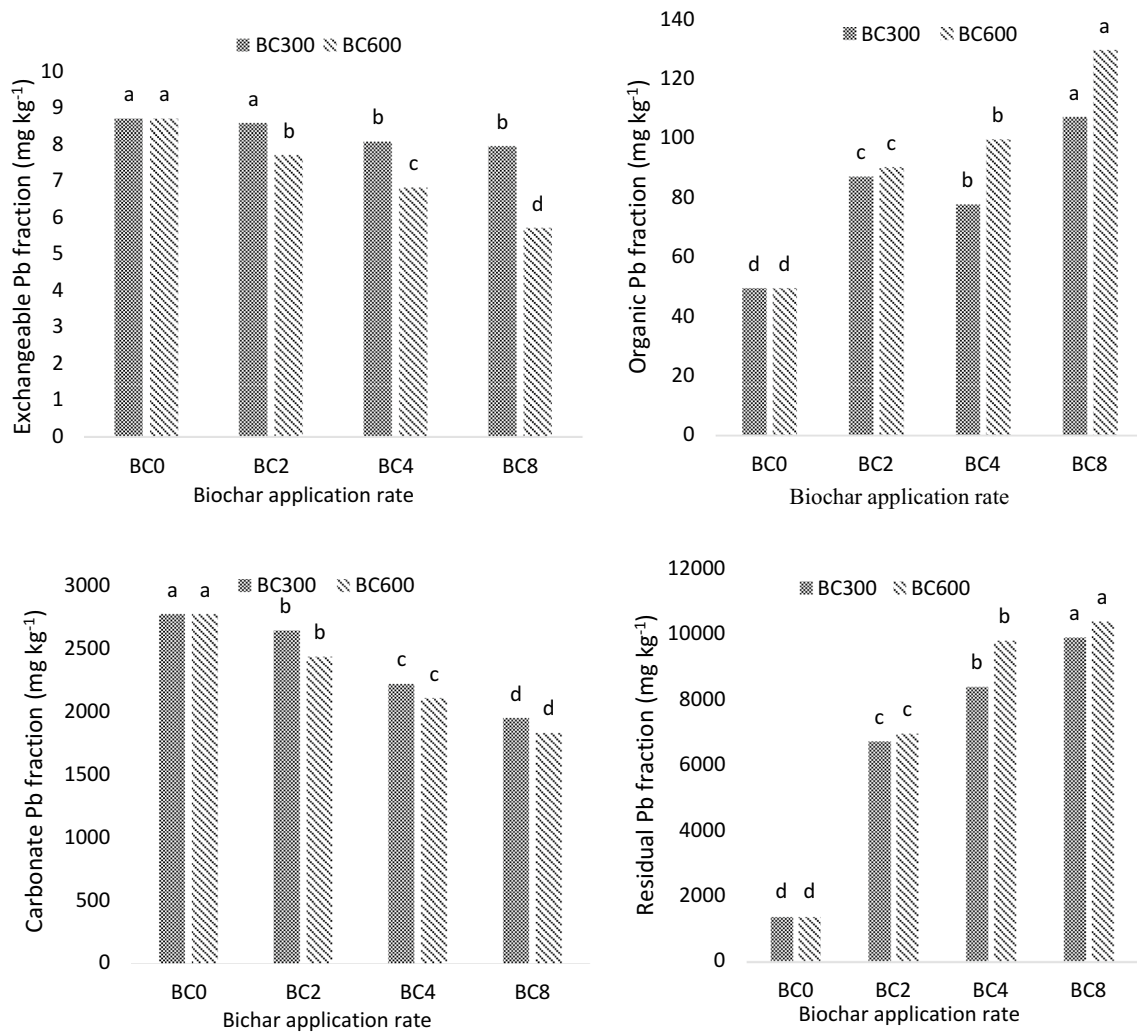
heavy metal content of the soil; however, it reduced the Cd and Pb bioavailability and mobility.

Park et al. [45] studied the effect of two biochars in a heavy-metal-spiked soil and a naturally strongly polluted soil. They executed a sequential extraction of some heavy metals. They discovered that chicken manure biochar was effective on reducing only the extractable concentrations of Cd and Pb, while green waste biochar was more active in lessening all of the heavy metals studied. The bonded to organic matter heavy metal fractions were amplified after the biochar addition.

## Conclusions

The results revealed that the biochar produced from sewage sludge could efficiently decrease soil pH and EC value; change the speciation of Pb and Cd; decrease the contents of soil exchangeable Pb and Cd; and increase residual fraction. Moreover, these biochars may result in conversions of available forms of Pb and Cd into more chemically stable forms, with the consequent reduction of their mobility and bioavailability. It is noteworthy that the influence of biochar





**Fig. 6** Effect of the biochar application rate produced at the temperatures of 300 and 600 °C on the concentration of Pb in the soil fractions under controlled laboratory conditions. (BC<sub>0</sub>=no biochar added

as control; BC<sub>2</sub>=applied 2% biochar; BC<sub>4</sub>=applied 4% biochar; BC<sub>8</sub>=applied 8% biochar). Bars that do not share a common letter represent values that are significantly different at  $P \leq 0.05$

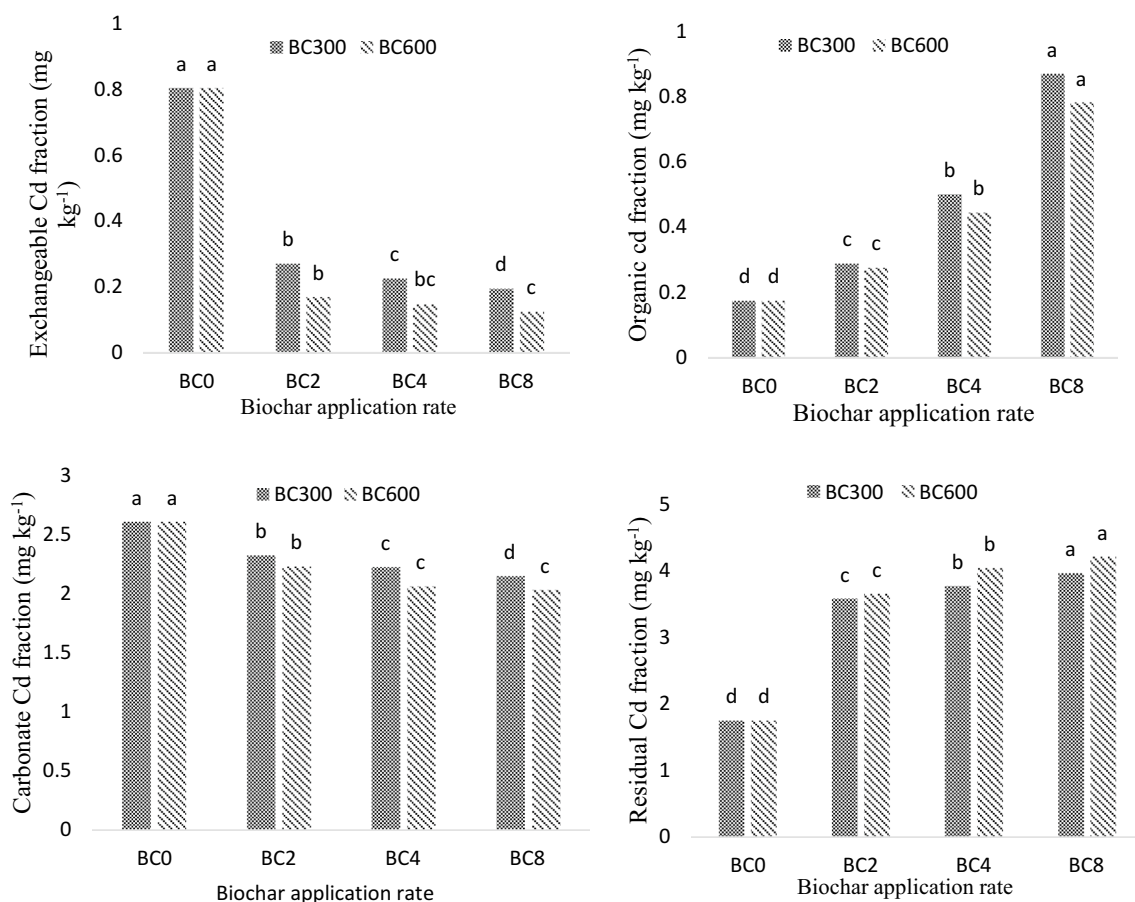
**Table 7** Effect of the biochar application rate produced at the temperatures of 300 and 600 °C on the fractionation of Cd

Extractable Pb fractions	Sources of variation	df	BC300		BC600	
			MS	P	MS	P
EXC	Biochar application rate (BC)	3	0.249	0.000	0.333	0.000
	Error	8	0.000		0.000	
ORG	Biochar application rate (BC)	3	0.283	0.000	0.212	0.000
	Error	8	0.000		0.000	
CAR	Biochar application rate (BC)	3	0.120	0.000	0.209	0.000
	Error	8	0.000		0.001	
RES	Biochar application rate (BC)	3	3.136	0.000	3.854	0.000
	Error	8	0.001		0.001	

df degrees of freedom, P probability level, MS mean square

on Pb and Cd mobility and bioavailability was altered by changing the pyrolysis temperature. Our findings demonstrated that biochar produced at 600 °C had a much smaller

microporous area and volume compared to the one produced at 300 °C. Therefore, the presence of more pores in the biochar produced at 600 °C could have affected the adsorption



**Fig. 7** Effect of the biochar application rate produced at the temperatures of 300 and 600 °C on the concentration of Cd in the fractions of the soil under controlled laboratory conditions. (BC<sub>0</sub>=no biochar

added as control; BC<sub>2</sub>=applied 2% biochar; BC<sub>4</sub>=applied 4% biochar; BC<sub>8</sub>=applied 8% biochar). Bars that do not share a common letter represent values that are significantly different at  $P \leq 0.05$

of Pb and Cd, and hence reduced their exchangeable form. The present study indicated that pyrolysis could be regarded as a promising sewage sludge treatment method for heavy metals immobilization in soil, and highlighted its potential in minimizing the harmful effects of biochar by controlling pyrolysis temperature. As the metals in the amended soil were gradually stabilized; application of biochar can be recommended for remediation of soil polluted with heavy metals.

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