EFFECT OF BIOCHAR ON CADMIUM, NICKEL AND LEAD UPTAKE AND TRANSLOCATION IN MAIZE IRRIGATED WITH HEAVY METAL CONTAMINATED WATER

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Abstract. This study was conducted to investigate the effect of biochar on bioavailability reduction of cadmium (Cd^{+2}), nickel (Ni^{+2}), and lead (Pb^{+2}) and its subsequent effects on soil properties and maize plant growth in a soil which was irrigated by contaminated water with above heavy metals. Twelve different biochar were prepared under two temperatures of 500 °C and 700 °C by using six biomass including residuals of wheat (WB), chickpea (CB), maize (MB), reed (RB), olive (OB) and sugarbeet (SB). Physicochemical properties of biochar including product percentage, percentage volatile matter, ash, pH, electrical conductivity (EC), cation exchange capacity (CEC), specific surface, and organic carbon (OC) were studied as well. Subsequently, the effects of 3 biochar selected under 700 °C (MB_{700}, RB_{700}, WB_{700}) at the levels of 0%, 2%, and 4% were employed for pot experiments. The results showed that higher level of temperature significantly ($P < 0.05$) increased pH, EC, ash percentage, specific surface area, and OC content of soil however Cd, Ni, and both shoot and root dry biomass decreased. This study results indicated that high application of biochar significantly decreased leaf area, and also shoot and root biomass.
Keywords: *maize, contaminated water, volatile matter, heavy metal, biochar*

Introduction

Soils are increasingly become contaminated by accumulation of heavy metals through applying urban and industrial sewage sludge along with chemical fertilizers (Hejazizadeh et al., 2016). In developing countries due to expanding of population, food demand is driving up which in turn increases the resources application and subsequently resulted in rising accumulation of Cd, Ni, and Pb in soils. Long term application of sewage sludge even with low concentration of heavy metals can also result in accumulation of these metals in soils (Lu et al., 2015). Low availability of water due to population increment, climate change and climate pollution has been turned into one of the major environment problems (Yao et al., 2012). Accumulation of heavy metal in soils is not only a serious threat for plants but also is a potential danger to human health as well (Hejazizadeh et al., 2016). Heavy metal should be of more concern as in contrast to organic matters, they do not decompose (Ingole and Tale, 2016).

In recent decade, biochar has gained more attention as their capability of carbon sequestration mitigates global warming, enhances soil fertility and reduces both organic and inorganic pollutants of soil (Zheng et al., 2013). Biochar is a carbonaceous material product of organic waste under oxygen-limited or fully depleted oxygen condition

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(Zhao et al., 2017; Lehmann, 2007). Physicochemical properties of biochar depend on starting material and applied temperature and by increasing temperature beyond 550 °C, specific surface area and aromatic components of biochar would increase (Elzobair, 2013). Biochar can also reduce the pollutants movement and thus prevent their uptake by crops (Yao et al., 2012). Different characters of biochar (due to feedstock or pyrolysis conditions) can enforce different impacts on soils fertility and crop production (Paneque et al., 2016). Various studies have indicated that biochar positive effects on environment and for crop production it depends on biochar feedstock and its production conditions (da Silva et al., 2017). Most of published results are originated from tropical, subtropical, and temperate regions but the impact of biochar in Mediterranean regions with hot and dry summers containing calcareous soils has not been fully realized yet (Paneque et al., 2016).

This study was conducted to investigate the effect of biochar on bioavailability reduction of cadmium (Cd^{+2}), nickel (Ni^{+2}), and lead (Pb^{+2}) and its subsequent effects on soil characteristics and corn plant growth in a soil which was irrigated by contaminated water with above heavy metals.

Materials and methods

This experiment was conducted as factorial based on complete random design with three replications in Anahita soil-plant-water analysis lab of Kermanshah state (Iran) in 2017. Twelve different biochars were prepared under two temperatures of 500 °C and 700 °C by using six starting biomass including residuals of wheat (WB_{500}, WB_{700}), chickpea (CB_{500}, CB_{700}), maize (MB_{500}, MB_{700}), reed (RB_{500}, RB_{700}), olive (OB_{500}, OB_{700}) and sugarbeet (SB_{500}, SB_{700}) to study the physicochemical properties of biochars. All feedstocks were dried in oven at 60 °C for 24 h and then were placed in electric furnace (Shimifan Model F. 47, Iran) for 2 h with warming rate of 8 °C min^{-1} under oxygen-limited conditions. After pyrolysis, when materials temperature equals to room temperature, they were weighed and after grinding them for physicochemical experiments, they were passed through 0.5 mm mesh. The physicochemical properties included yield%, ash%, pH, EC, CEC, specific surface area, assimilated carbon%, volatile material% elements (CHNO) analysis, and molar ratio of H/C and O/C. The study results were analyzed using SAS 9.3 and means were compared based on LSD. Due to high importance of specific surface area, porosity and CEC in metal pollutants reductions (Komkiene and Baltrenaits, 2016) three biochars with high specific surface area and high CEC and oxygen factor groups like carboxyl and hydroxyl groups were chosen for pot experiments. Biochars MB_{700}, WB_{700}, and RB_{700} were final selections.

Pot experiment

In order to find the impacts different amounts of selected biochars (MB_{700}, WB_{700}, and RB_{700}) on soil physicochemical properties (pH, EC, OC, amount of cadmium, nickel, and lead in soil and plant materials) and plant properties (leaf area, root and shoot dry matter), a pot experiment was conducted in June 2017, as factorial based on complete random design with three replications in Mahidasht Research Center in Kermanshah (Iran). The study results were analyzed using SAS 9.3 and means were compared based on LSD.

About 82 kg soil, classified as fine mixed thermic typic calcixerepts, was used to fill the pots and a sample of soil was used to determine its physicochemical properties.

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Each pot (250 mm height and 240 mm diameter) was filled by 3 kg soil. The selected three biochars at same level were added to pots. Preventing soil wash by irrigation, plastic nets were applied at the bottom of each pot. Three seeds corn (Zea mays L.) were planted at depth of 5 mm in each pot. All pots were irrigated up to field capacity by polluted water with Cd, Ni, and Pb at 1000, 2000, and 3000 microgram per liter, respectively, for two months. Ten days after emergence, two of seedlings were removed, and plants were harvested two months after sowing. At final harvest, leaf area was measured by leaf area meter (CID Bio-Science model CI-202, USA). After harvest, shoots and roots were separated, roots were washed by tap water and then by deionized water to remove soil and any remained biochar. Both shoots and roots were dried at 60 °C till to get a constant weight and then were grinded. Finally, a soil sample was taken from each pot.

Analysis of biochar physicochemical properties

Biochar production was obtained as (Sadaka et al., 2014; Zhao et al., 2017) the ratio of biochar weight to initial material weight (dried at 60 °C) and percentage of volatiles and ash were determined at two temperatures of 750 °C and 950 °C according to the procedure of American Society for Testing and Material (ASTM). To measure the pH, biochar was mixed with deionized water as ratio (W/V) of 1:20 then was on shaker for 1.5 h (Rajkovich et al., 2012) and finally samples were taken to determine pH by using pH meter (Metrohm model 691, Switzerland).

Biochar was mixed with deionized water as ratio of 1:10, was on shaker for 1 h and then by using conductivity meter (Jenway model 4010, UK) electrical conductivity was determined (Yang et al., 2015). Cation exchange capacity was determined by using NH4OAC solution (Melo et al., 2013; Song and Guo, 2012) and specific surface area was determined based on Brunauer-Emmett-Teller (BET) method (Brunauer et al., 1937). Biochars functional group were studied using Fourier-transform infrared (FTIR) spectrometer (Bruker model vertex 70, Germany) at wavelengths of 500-4000 nm. Biochar elemental composition (CHN) was measured by elemental analyzer (Costech model ECS4010, Italy). Oxygen percentage was calculated as:

$$O\ (\%) = 100 - (C\% + H\% + N\% + Ash\%)$$

and molar element ratios, O/C and H/C were calculated as well. Nutrients of MB_{700}, RB_{700}, WB_{700} samples including P, K, Ca, Mg, Zn, Fe, and trace elements (Pb, Ni, and Cd) were measured using peroxide hydrogen (H_2O_2 digestion) and sulfuric acid (H_2SO_4) (Wolf, 1982). All samples were tested by atomic absorption (Perkin Elmer Model 1100 D) while Na and K were tested by flame photometer (Jenway model PFP7, UK) and P by spectrometer (Apel Model PD303S, Japan).

Soil physicochemical properties analyses

Soil pH was determined by using paste saturation method (Metrohm 691, Switzerland pH meter) and EC were measured using EC meter (Jenway model 4010, UK). Phosphorous was measured according to Olsen method by using a spectrophotometer, (Apel model PD 303S, Japon) and potassium (ammonium acetate extract) was determined using a flame photometer (Jemway model PFP7, Japon). Organic carbon (wet ash method) and total neutralization value (TNV %) ($CaCO_3$) were measured using neutralization with

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1N HCl. The bioavailable Cd, Ni and Pb content of soil were determined by DTPA method (0.005 mol L^{-1} DTPA and 0.01 mol L^{-1} $CaCl_2$ and 0.01 mol L^{-1} triethylamine) (Lindsay and Norvell, 1978) using an atomic absorption spectrophotometer (Perkin-Elmer model 1100 D, USA).

Feedstock and maize plant analysis

All elements including the heavy metals of feedstock samples and maize plant shoots and roots were measured using dry ash and digest in HCl extraction methods by flame photometer and spectrophotometry and atomic absorption.

Results and discussion

Biochar properties

Biochar properties (*Table 1*) showed that with increasing temperature from 500 °C to 700 °C biochar production reduced but their ash increased. This is consistent with Rajkovich et al. (2012) study. Low production of biochar due to high temperature may be due to cracking of organic matter and gases drift (Zhang et al., 2015). In this study the highest production (34.17%) was for WB_{500} and in the second rank was CB_{500} by 33.93%. Results also showed that increasing temperature (pyrolysis temperature) significantly reduced volatile matter percentage (*Table 1*), which is consistent with Rajkovich et al. (2012). Reduction of volatile matter percentage can be due to water loss and organic material (cellulose, hemicellulose, and lignin) decomposition during pyrolysis (Sadaka et al., 2014). Increasing pyrolysis temperature significantly ($P < 0.05$) increased pH and EC as well (*Table 1*). Similarly, Jindo et al. (2014) reported that increasing temperature to 700 °C increased the biochar. Samples of pH and EC were 9.06-10.14 and 167.7-760 mS/m respectively. Increasing pH and EC may be due to increasing of ash (Wu et al., 2012; Paz-Ferreiro et al., 2014; da Silva et al., 2017; Novak et al., 2009).

Table 1. *Physical and chemical characteristic of biochars (values are mean of three replications)*

	Yield (%)		pH		Dry ash (%)		VM (%)		Fixed carbon (%)		EC (mS m^{-1})		BET (m^2 g^{-1})		CEC (Cm kg^{-1})	
Biochar	**500 °C**	**700 °C**	**500 °C**	**700 °C**	**500 °C**	**700 °C**	**500 °C**	**700 °C**	**500 °C**	**700 °C**	**500 °C**	**700 °C**	**500**	**700 °C**	**500 °C**	**700 °C**
WB	34.17^{a}	29.07^{cd}	9.39^{bcd}	10.13^{a}	25.86^{b}	29.91^{a}	40.57^{c}	32.28^{e}	33.57^{g}	38.05^{f}	410.0^{e}	578.3^{c}	4.14^{g}	142.2^{b}	16.17^{f}	20.52^{cd}
RB	27.80^{d}	25.70^{e}	9.06^{d}	9.74^{abc}	8.98^{gh}	12.48^{f}	43.97^{b}	36.05^{d}	47.05^{de}	51.47^{c}	410.3^{e}	462.3^{d}	3.29^{g}	241.1^{a}	12.86^{g}	19.77^{cd}
MB	29.53^{bcd}	25.17^{e}	9.35^{cd}	9.97^{a}	9.50^{g}	12.47^{f}	43.20^{bc}	24.84^{gh}	47.30^{de}	62.69^{b}	167.7^{g}	214.3^{f}	5.28^{g}	97.89^{c}	18.90^{de}	21.60^{bc}
CB	33.93^{a}	30.00^{bc}	9.41^{bcd}	10.14^{a}	15.70^{e}	22.16^{c}	47.90^{a}	27.48^{fg}	36.40^{fg}	50.36^{cd}	540.0^{c}	760.0^{a}	3.41^{g}	23.17^{e}	22.84^{b}	11.01^{g}
OB	29.70^{bc}	27.80^{d}	9.14^{d}	9.78^{ab}	7.47^{h}	9.75^{g}	28.20^{f}	21.70^{h}	64.33^{b}	68.55^{a}	206.0^{fg}	398.7^{e}	6.64^{g}	82.39^{d}	17.25^{ef}	11.47^{g}
SB	31.20^{b}	24.70^{e}	9.30^{d}	10.08^{a}	17.89^{d}	15.36^{e}	35.93^{d}	31.59^{e}	46.18^{e}	53.05^{c}	400.3^{e}	631.3^{b}	3.40^{g}	11.18^{f}	25.78^{a}	11.82^{g}
LSD (5%)	1.78		0.43		1.62		3.33		3.90		39.92		4.12		1.98	

Different letters indicate significant differences between treatments $P < 0.05$

BET and CEC results (*Table 1*) indicated that specific surface and CEC of biochars (WB, RB and MB) significantly increased as the temperature increased from 500 °C to 700 °C. Increase of biochar specific surface due to high temperature can be the result of organic matter degradation and developing pores and channels in biochar during pyrolysis (Zhao et al., 2017) and CEC increase can be due to change of negative charge

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in relation to pH (da Silva et al., 2017) and specific surface area rise. Komkiene and Baltrenaite (2016) resulted that by increasing temperature from 450 °C to 700 °C specific surface area of two types of biochar increased from 9.6 to 10.4 and 5.92 to 7.17 $m^2 g^{-1}$ which is similar to this study results.

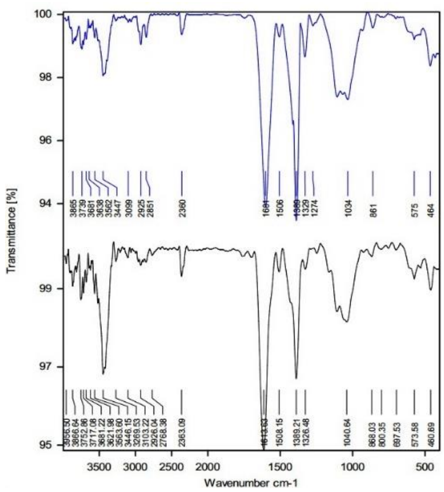
Elemental analysis and determination of ratios O/C and H/C are most important indices for realization of aromaticity and maturity of biochars (Schmidt and Noack, 2000; Nguyen and Lehmann, 2009). Results of analysis (*Table 2*) showed that by increasing pyrolysis temperature, carbon percentage of biochar samples increased while H, N, O and ratios H/C, O/C reduced. Reduction of O and H can be the result of removal of water and oxygen from hydroxyl and carboxyl agents (Wang et al., 2015). The highest (84.75%) and lowest (43.19%) carbon percentage were from OB_{700} and SB_{500} respectively. Melo et al. (2013) and Jindo et al. (2014) showed that by increasing pyrolysis temperature from 500 °C to 700 °C, carbon%, hydrogen%, N% and molar ratio of H/C and O/C of biochar increased as well which are also consistent with our results.

Table 2. *Elemental analysis of biochars, H/C and O/C ratios (values are mean of three replications)*

	N		**C**		**H**		**O***		**H/C**		**O/C**	
	%								**Molar ratio**			
Biochar	**500 °C**	**700 °C**	**500 °C**	**700 °C**	**500 °C**	**700 °C**	**500 °C**	**700 °C**	**500 °C**	**700 °C**	**500 °C**	**700 °C**
WB	0.67^{b}	0.35^{def}	54.12^{f}	60.84^{de}	2.60^{a}	1.25^{d}	20.33^{d}	8.48^{g}	0.58^{a}	0.25^{c}	0.28^{d}	0.10^{gh}
RB	0.47^{cd}	0.28^{f}	55.11^{f}	75.80^{b}	2.60^{a}	1.39^{d}	33.42^{b}	10.82^{f}	0.56^{a}	0.22^{cd}	0.45^{b}	0.11^{g}
MB	0.82^{a}	0.41^{cde}	68.91^{c}	78.22^{b}	2.72^{a}	1.81^{c}	18.6^{e}	7.80^{gh}	0.47^{b}	0.28^{c}	0.20^{f}	0.07^{i}
CB	0.89^{a}	0.48^{c}	63.09^{d}	70.13^{c}	2.67^{a}	1.25^{d}	18.2^{e}	6.75^{hi}	0.51^{ab}	0.21^{cd}	0.22^{e}	0.07^{i}
OB	0.88^{a}	0.38^{cdef}	59.25^{e}	84.75^{a}	2.23^{b}	1.85^{c}	30.73^{c}	5.40^{i}	0.45^{b}	0.26^{c}	0.39^{c}	0.05^{j}
SB	0.79^{ab}	0.31^{ef}	43.19^{g}	75.33^{b}	1.82^{c}	1.06^{d}	36.89^{a}	8.70^{g}	0.51^{ab}	0.17^{d}	0.64^{a}	0.09^{h}
LSD (5%)	0.125		3.305		0.361		1.663		0.072		0.014	

*Determined by difference. Different letters indicate significant differences between treatments $P < 0.05$

FTIR spectrum of selected biochar at two different temperatures are presented in *Figure 1*.



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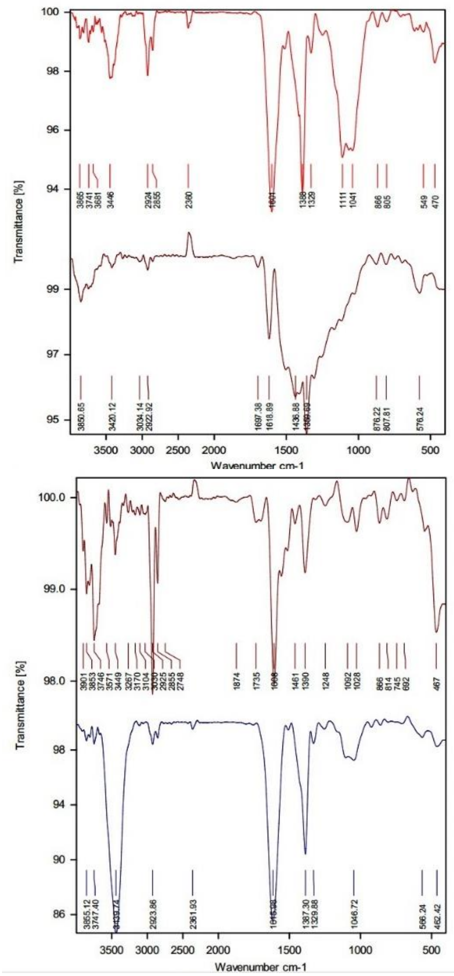

Figure 1. *Biochar spectrum for MB, RB, and WB*

As temperature increased a reduction of O-H stretching (3680 cm^{-1}) was observed within FTIR spectrum which may be due to dehydration of biomass and reduction of polarity during pyrolysis.

Effect of biochar on soil pH, EC and OC

The results indicated that the effect of biochar type (*Table 3*) and amount were significant on soil pH, OC and EC (*Fig. 2A*, *B*, *C*). Comparison of means showed that WB_{700} was more effective in increasing soil pH compared to MB_{700} or RB_{700} (*Table 3*). WB_{700} and MB_{700} significantly ($P < 0.05$) increased soil EC and OC (*Table 3*). Although the effects of MB_{700} and RB_{700} on soil OC were similar, these biochars were more effective than WB_{700}. Similarly, there was no significant ($P < 0.05$) difference between WB_{700} and RB_{700} in terms of soil EC, but these biochars were more effective than MB_{700}. Results showed (*Tables 1* and *4*) that biochars pH were 10.13, 9.74, and 9.97 for WB_{700}, RB_{700} and MB_{700}, respectively, whereas soil pH was 7.52. Therefore, it should be expected that soil pH may increase as a result of biochar application in soil. Albuquerque et al. (2011) and Xu (2012) showed that adding biochar to soil increased the pH. da Silva et al. (2017) showed that adding 3 biochar types at highest amount into

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the soil not only increased pH by 0.76 to 1.68, but also soil organic carbon content also linearly increased. These results are consistent with this study results. Soil pH increase may be due to high biochar ash and its components. The ash product from pyrolysis contains oxide and hydroxide of alkali metals which are easily dissolve in water and are able to increase soil pH (da Silva et al., 2017). Further to ash, type of feedstock has also shown effects on pH and EC (Qayyum et al., 2015; Abdelhafez et al., 2014). Qayyum et al. (2015) showed that from 9 different biochars, 5 of them were able to increase soil EC, 3 of them increased soil pH and one did not show any significant ($P < 0.05$) effect on soil pH and EC. Biochars properties depend on factors such as feedstock type, feedstock size, pyrolysis temperature and retention time in oven (Paz-Ferreiro et al., 2014). In our study increasing biochar dose (*Fig. 2A*, *B* and *C*) led to increasing soil pH, EC and OC (except MB_{700} for EC). Similary, some studies have shown that increasing biochar dose would increase soil organic matter (Dume et al., 2016; da Silva et al., 2014) as well as soil EC (Abdelhafez et al., 2014; Yang et al., 2015).

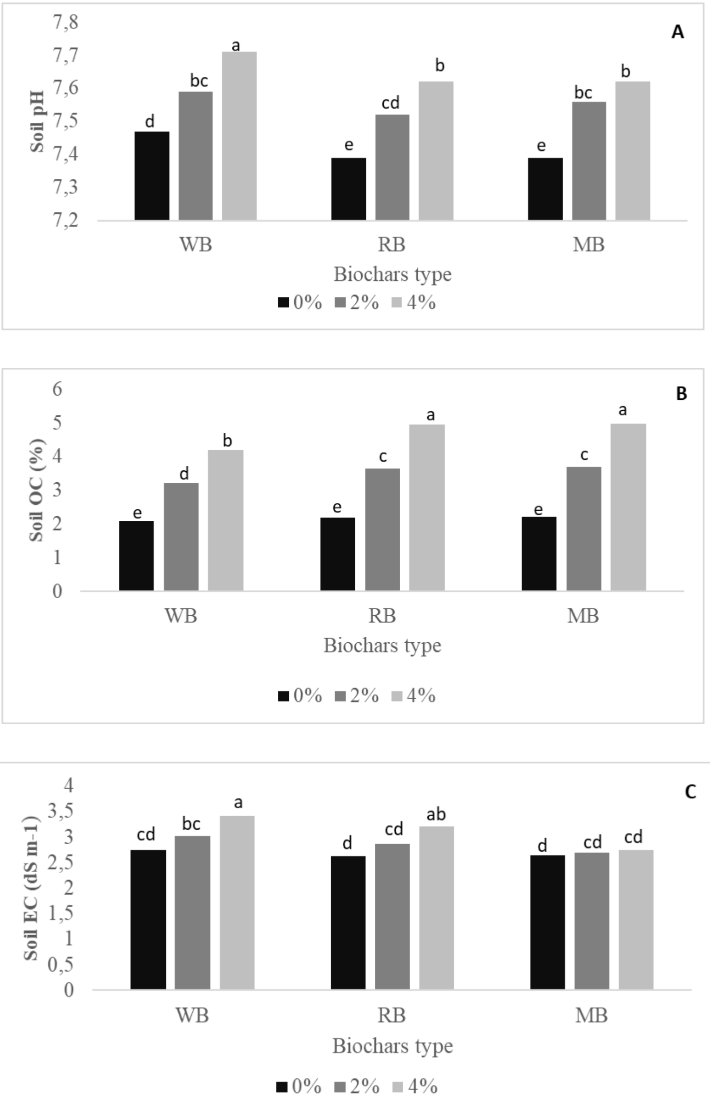

Figure 2. *Effect of different rates of biochars on soil pH (A), OC (B) and EC (C)*

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Table 3. *Effect of biochar types on shoot, root, soil properties, plant indices and translocation factor (values are mean of three replications)*

Biochar types	Shoot			Root			Soil						Plant				TF value		
	Cd	Ni	Pb	Cd	Ni	Pb	Cd	Ni	Pb	pH	EC	OC	LA	Shoot	Root	R:S	TF_{Cd}	TF_{Ni}	TF_{Pb}
	mg kg^{-1}										dS/m	%	cm^2	gr					
WB	0.56^b	1.22^a	3.35^a	2.26^a	3.61^a	6.24^a	0.41^a	2.41^c	2.38^a	7.58^a	3.06^a	3.17^b	294.7^c	7.04^b	1.71^c	4.11^a	0.24^b	0.34^a	0.53^a
RB	0.60^a	1.24^a	2.75^b	2.25^a	3.60^a	6.36^a	0.41^{ab}	2.81^a	2.33^a	7.50^b	2.89^a	3.59^a	322.6^b	7.34^a	1.85^b	3.96^b	0.27^a	0.34^a	0.41^b
MB	0.57^b	1.23^a	2.69^b	2.03^b	3.68^a	6.20^a	0.39^b	2.56^b	2.33^a	7.52^b	2.70^b	3.62^a	330.8^a	7.37^a	1.87^a	3.93^b	0.28^a	0.31^b	0.41^b
LSD (0.01)	0.022	0.072	0.091	0.045	0.112	0.234	0.013	0.064	0.125	0.045	0.187	0.182	4.342	0.078	0.018	0.045	0.012	0.018	0.012

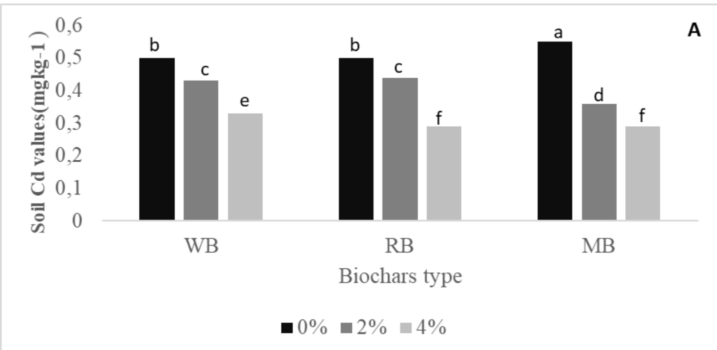
Different letters indicate significant differences between treatments $P < 0.05$

Table 4. *Soil physicochemical analyses*

pH	EC	TNV	OC	N	P	K	Mn	Fe	Zn	Cu	Cd	Ni	Pb
	dS/m	%			mg kg^{-1}								
7.52	2.12	32.5	2.19	0.22	21	1120	23.4	11.40	4.12	2.34	0.31	1.51	2.1

Effect of biochar on bioavailability of Cd, Ni and Pb in soil

Mean comparison (*Table 3*) showed that biochar types differ in their reducing effect on Cd and Ni bioavailability, whereas there was no significant ($P < 0.05$) difference between them for effect on Pb. The amended soil with MB_{700} showed less bioavailable Cd in comparison to WB_{700} or RB_{700}. There was no significant ($P < 0.05$) difference between WB_{700} and RB_{700}. The effect of WB_{700} in reducing soil bioavailable Ni concentration was more pronounced compared to RB_{700} or MB_{700}. Increasing biochar does significantly ($P < 0.05$) decreased bioavailable Cd, Ni, and Pb compared to control (0.00% application) (*Fig. 3A*, *B* and *C*). In comparison with control, application of 4% biochar decreased bioavailable Cd, Ni, and Pb by 58.8%, 46% and 76%, respectively. Increasing soil pH may lead to Cd precipitation as Cd (CO_3) (Mousavi et al., 2011) and lead to precipitation as pb5 $(PO_4)_3Cl$ (Kopittke et al., 2008). In addition, increasing soil pH increases binding metal ions by pH dependent surface ligands (Uchimiya et al., 2011). The effect of biochar depends highly on the type of pollutant metal (Uchimiya et al., 2010). Lead in soil highly depends to organic matter and by increasing pH, lead stability (Karami et al., 2011) and also Cd and Ni stability (Yang et al., 2015) will increase. According to Park et al. (2011) and Fellet et al. (2011) adding biochar to soil decreases bioavailability of Cd and Pb of soil. Similar to this study results, Cui et al. (2011) also reported lower Cd of soil as biochar was added to soil.



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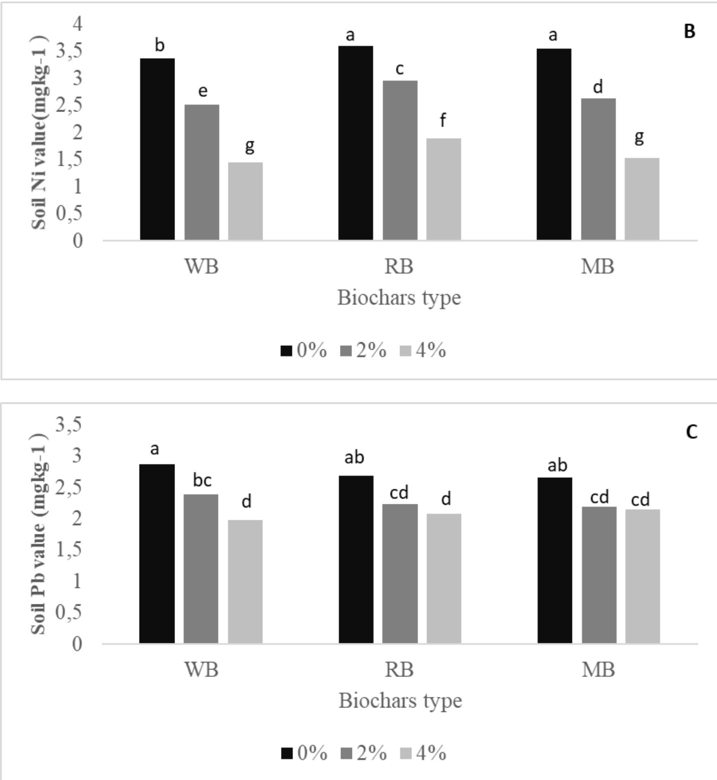

***Figure 3.** Effect of different rates of biochar different rates on soil bioavailable Cd (A), Ni (B) and Pb (C)*

The feedstock and three types of biochar (WB_{700}, RB_{700}, and MB_{700}) analysis (*Tables 5* and *6*) indicated that P, Na, Ca, and Mg content in biochar are more compared to feedstocks. In addition, the soil Ca and P content were also high (*Table 4*). Increasing P availability due to biochar application plays a key role in Pb stabilization in water solution (Cao et al., 2009) and lead stabilization through precipitation or in complex with phosphate (Ahmad et al., 2014). Simultaneous release of elements Na, Ca, K, Mg, P, and S from soil and biochar can result in stability of heavy metals (Uchimiya et al., 2011). In this study, WB_{700}, RB_{700}, and MB_{700}, had O-containing functional groups (*Fig. 1*). These functional groups increase biochar effect (Yang et al., 2015; Ahmad et al., 2014) therefore they should be more effective for heavy metal stabilization especially in acidic soils with low CEC and organic matter (Uchimiya et al., 2011).

***Table 5.** Chemical analyses of three types of feedstocks*

Feedstock	Cd	Ni	Pb	Cu	Zn	Fe	Mn	N	P	K	Ca	Mg
	mg kg^{-1}							%				
Wheat residual	0.23	1.14	1.38	10.8	25	80	18	1.22	0.16	1.10	0.33	0.18
Reed (leave and stalk)	0.1	1.0	0.90	8.3	23	65	13	1.03	0.11	0.92	0.37	0.25
Maize residual	0.27	1.25	1.61	14.7	32	87	25	2.12	0.25	1.42	0.30	0.21

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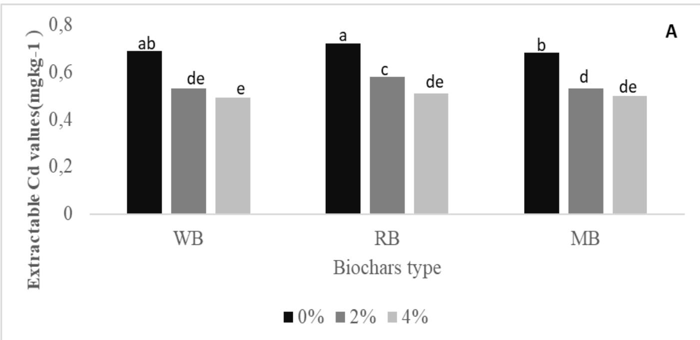
Table 6. *Chemical composition of biochar*

Biochar	Cd	Ni	Pb	Cu	Zn	Fe	Mn	P	K	Ca	Mg	Na
	mg kg^{-1}							g kg^{-1}				
WB700	0.63	2.2	2.1	20	85	360	156	3.6	29.7	8.2	6.5	6.8
RB700	0.27	1.1	1.3	17	73	310	148	3.0	18.8	10.4	7.8	5.7
MB_{700}	0.71	2.6	2.7	27	89	395	175	4.2	38.0	9.0	6.9	4.9

Effect of biochar on Cd, Ni, and Pb uptake and translocation by maize

Means comparison (*Table 3*) indicated that there was no significant difference between MB_{700} and WB_{700} biochars for Cd reduction in maize shoots but their effect was higher than RB_{700}. In addition, this study results indicated that there was no significant difference between MB_{700} and RB_{700} for reducing Pb in maize shoots, however their effect was less than WB_{700}. For reduction of Ni in shoots, results showed no significant ($P < 0.05$) difference between biochars. This study revealed that Cd, Ni, and Pb concentrations significantly ($P < 0.05$) decreased in both shoot and root of maize as biochar application increased (*Fig. 4A, B, C*). Kacálková et al. (2014) reported that increasing heavy metal concentration in soil increased their uptake by plants (Komkiene and Baltrenaite, 2016) also found that application of adsorbent materials into the soil decrease heavy metal uptake by plants. Reduction of metal concentration in plants due to biochar application may be related to immobilization of bioavailable metals and dilution effects of increased biomass (Park et al., 2011). In this study highest uptake of Cd, Ni and Pb by corn plants was monitored when no biochar was applied into the soil while by adding 4% biochar the uptake of these metals was at minimum level. By increasing amount of biochar application, concentration of Cd, Ni and Pb in plants reduced (*Fig. 4A, B, C*). Similarly, Jatav et al. (2016) showed that maximum and minimum uptake of Cd, Ni and Pb were respectively obtained by only applying 30 t/ha of sewage sludge and 20 t/ha biochar plus 30 t/ha of sewage sludge. Increasing the amount of applied biochar reduced in heavy metal uptake. Al-Wabel et al. (2015) showed that 5% biochar application reduced heavy metal (Cu, Zn, Mn, and Cd) in corn plants.



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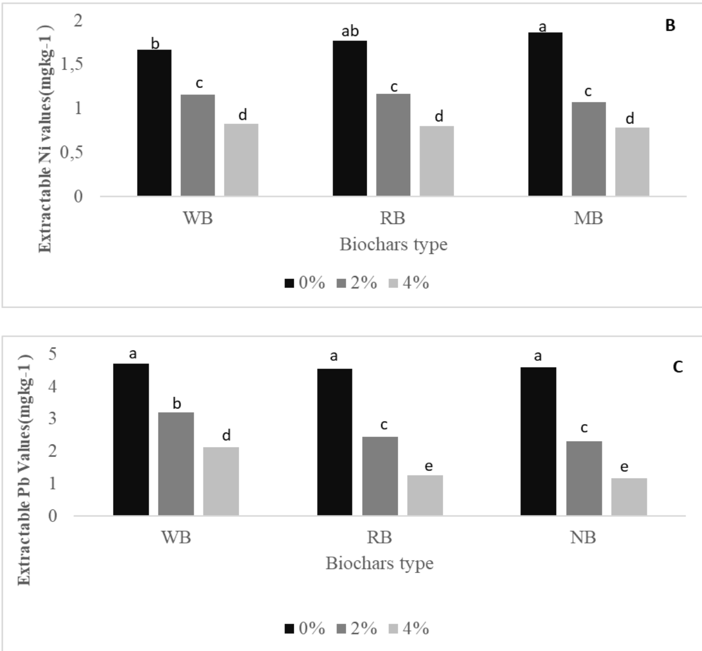

Figure 4. *Effect of different rates of biochar different rates on shoot extractable Cd (A), Ni (B) and Pb (C)*

Among higher plants, there are two groups of plants that can tolerate high concentrations of heavy metals: excluder plants and accumulator plants. The former is able to inhibit heavy metal transport into the plants whereas the later uptake heavy metals and accumulate them in different parts for example, roots or shoots (Lu et al., 2015). In this study, translocation factor (TF) was determined by using the ratio of heavy metal concentration in shoots to roots ($TF=C_{shoot}/ C_{root}$) (Bu-Olayan and Thomas, 2009). Statistical analyses showed that TF value was affected by biochar type and amount (*Table 3* and *7*). The minimum TF_{Cd} (0.23) was related to $WB_{2\%}$ whereas the minimum TF_{Ni} (0.28) and TF_{Pb} (0.33) were related to $MB_{2\%}$ and $MB_{4\%}$ respectively. Accumulator plants can be identified by TF > 1 whereas excluders can be recognized by TF < 1 (Shumaker and Begonia, 2005). The results demonstrated that TF values for Cd, Ni and Pb were less than 1.

Table 7. *Effect of different rates of biochars on shoot, root, soil properties, plant indices and translocation factor (values are mean of three replications)*

Biochar	Rate	Shoot			Root			Soil						Plant				TF value		
		Cd	Ni	Pb	Cd	Ni	Pb	Cd	Ni	Pb	pH	EC	OC	LA	Shoot	Root	R:S	TF_{Cd}	TF_{Ni}	TF_{Pb}
		mg kg^{-1}										dS/m	%	cm^2	gr					
WB	R_0	0.69^{ab}	1.67^{b}	4.73^{a}	2.45^{b}	4.71^{a}	8.48^{a}	0.50^{b}	3.38^{b}	2.78^{a}	7.47^{d}	2.75^{cd}	2.10^{e}	326.7^{d}	7.35^{b}	1.82^{c}	4.03^{b}	0.28^{a}	0.35^{bc}	0.55^{a}
	$R_{2\%}$	0.53^{de}	1.16^{c}	3.21^{b}	2.26^{c}	3.63^{b}	6.34^{b}	0.4^{c}	2.51^{e}	2.39^{bc}	7.59^{bc}	3.02^{bc}	3.23^{d}	294.8^{ef}	7.07^{c}	1.71^{e}	4.13^{a}	0.23^{c}	0.32^{b}	0.50^{b}
	$R_{4\%}$	0.49^{e}	0.83^{d}	2.14^{d}	2.08^{d}	2.38^{c}	3.91^{cd}	0.33^{e}	1.44^{g}	1.98^{d}	7.71^{a}	3.42^{a}	4.19^{b}	262.7^{g}	6.73^{d}	1.61^{f}	4.19^{a}	0.24^{bc}	0.37^{ab}	0.55^{a}
RB	R_0	0.72^{a}	1.77^{ab}	4.54^{a}	2.60^{a}	4.64^{a}	8.56^{a}	0.50^{b}	3.60^{a}	2.69^{ab}	7.39^{e}	2.62^{d}	2.20^{e}	349.8^{b}	7.46^{ab}	1.90^{ab}	3.92^{de}	0.28^{a}	0.37^{ab}	0.54^{a}
	$R_{2\%}$	0.58^{c}	1.18^{c}	2.44^{c}	2.10^{d}	3.69^{b}	6.52^{b}	0.44^{c}	2.95^{c}	2.23^{cd}	7.52^{cd}	2.86^{cd}	3.64^{c}	329.9^{cd}	7.44^{ab}	1.88^{b}	3.97^{bcd}	0.28^{a}	0.32^{c}	0.38^{c}
	$R_{4\%}$	0.51^{de}	0.80^{d}	1.26^{e}	2.05^{d}	2.47^{c}	3.99^{c}	0.29^{f}	1.89^{f}	2.08^{d}	7.62^{b}	3.21^{ab}	4.96^{a}	288.2^{f}	7.13^{c}	1.78^{d}	4.02^{bc}	0.25^{b}	0.33^{c}	0.33^{e}
MB	R_0	0.68^{b}	1.86^{a}	4.57^{a}	2.38^{b}	4.71^{a}	8.59^{a}	0.55^{a}	3.54^{a}	2.65^{ab}	7.39^{e}	2.65^{d}	2.22^{e}	357.8^{a}	7.49^{a}	1.93^{a}	3.88^{e}	0.39^{a}	0.39^{a}	0.54^{a}
	$R_{2\%}$	0.53^{d}	1.07^{c}	2.31^{c}	1.96^{e}	3.76^{b}	6.67^{b}	0.36^{d}	2.63^{d}	2.19^{cd}	7.56^{bc}	2.70^{cd}	3.70^{c}	337.2^{c}	7.48^{ab}	1.89^{b}	3.94^{cde}	0.28^{a}	0.28^{d}	0.36d
	$R_{4\%}$	0.50^{de}	0.78^{d}	1.17^{e}	1.76^{f}	2.57^{c}	3.36^{d}	0.29^{f}	1.53^{g}	2.15^{cd}	7.62^{b}	2.75^{cd}	4.98^{a}	297.3^{e}	7.18^{c}	1.81^{c}	3.97^{bcd}	0.29^{a}	0.29^{d}	0.33^{de}
LSD (0.01)		0.035	0.098	0.138	0.098	0.240	0.285	0.036	0.196	0.219	0.069	0.346	0.219	16.82	0.208	0.03	0.170	0.069	0.020	0.033

Different letters indicate significant differences between treatments P < 0.05

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Effect of biochar on leaf area, shoot and root biomass

This study results indicated that the effects of biochar type were significant ($P < 0.05$) on leaf area, shoot and root biomass (*Table 3*). Comparison of means showed that MB_{700} caused the maximum leaf area (330.8 cm^2), shoot (7.37 g), and root biomass (1.93 g), respectively. The minimum leaf area (294.7 cm^2) and root biomass (1.61 g) were related to WB_{700}. This study results showed that leaf area, shoot and root biomass significantly decreased with increasing biochar application (*Table 7*). In current research, produced biochars showed different properties which resulted in different effects on soil (Paneque et al., 2016) and thus may result in different responses from plants (da Silva et al., 2017). Results analysis (*Table 6*) showed that Na concentration in biochars was 4900-6800 mg kg^{-1}. Increasing biochar dose can increase Na in soil. Rajkovich et al. (2011) reported that Na negatively (especially in low salty soil) affects maize growth, increases the soil osmotic potential and reduces the water uptake by plants. However, the liming effect of biochar is considered positive property for acidic soils but in soils with high pH, liming effect can have undesirable effects (Alburquerque et al., 2014). As well as Paneque et al. (2016) reported that large specific surface area of some biochars with high CEC and water holding capacity may have increased the competition for water which cuts down the potentially positive effect of biochar amendment.

Conclusion

Application of biochar in a semi-arid environment with high alkaline soil, high lime and rather low organic matter resulted in reduction of Cd, Ni, and Pb in both soil and plants however high level application of biochar, increased the pH and EC of the soil and reduced plants growth indices like leaf area and shoot and root biomass. Effects of MB_{700} was less than effects of WB_{700} and RB_{700} on the mentioned growth indices. To reduce the translocation of heavy metals to plants and biochar effects on growth indices, application of 2% or less from MB_{700} is recommended. Production of biochar with less EC and pH and suitable application dose in lime soils of semi-arid regions may be beneficial but requires more studies.

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