

IMPACT OF *Zea mays* L. WASTE DERIVED BIOCHAR ON CADMIUM IMMOBILIZATION AND WHEAT PLANT GROWTH

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The lethal consequence of cadmium (Cd) toxicity is a serious environmental concern in crops and food chain. Promising strategies for Cd immobilization are prerequisite to diminish its mobility through biochar. Present research highlights the laboratory and greenhouse-based study of production and quality assessment of biochar derived from maize (*Zea mays* L.) crop waste. Further, the effect of biochar on the growth of wheat plants under the cadmium stress was evaluated along with Cd bioaccumulation in shoots, roots, micro and macronutrients, and characterization of wheat plant roots grown in Cd-spiked soil. The biochar was prepared at 700°C in a muffle furnace heating for 2 hours under anaerobic conditions. Different concentrations of biochar (BC) i.e., 0%, 1.5%, and 3% w/w, along with three different rates of Cd levels: 0, 10, and 20 mg/kg were used in pot culture experiment. The physiological and morphological parameters were analyzed after 75 days of harvesting. Amendments of biochar increased plant dry biomass by 55% at BC 1.5% and 68% at BC 3%, while biochar enhanced fresh biomass by 21% at BC 1.5% and 25% at BC 3%. It also reduced Cd in wheat shoots by 51% at BC 1.5% and 48% at BC 3%. Similarly, Cd reduction was recorded in wheat roots by 23% at BC 1.5% and 51% at BC 3%. In addition, the maize derived biochar enhanced root length by 23% at BC 1.5% and 38% at BC 3%. Root surface area was enhanced by 39% at BC 1.5% and 92% at BC 3%, while root volume was increased by 54% at BC 1.5% and 72% at BC 3%. In summation, maize waste-derived biochar presented positive outcomes as soil amendments for enhancing the wheat plant growth and Cd immobilization and thus, reducing its bioavailability in the Cd-spiked soil to alleviate food security risks.

Keywords: Biochar, agro-waste, cadmium, immobilization, XRD, contaminants.

INTRODUCTION

The rapidly growing human population, climate change, infectious diseases and degradation of soil habitats have seriously affected the global food supply chain (Hofstra *et al.*, 2016). The demand for food is continued to grow with an order of magnitude. It has been estimated that the demand for food and agriculture products will be almost double in the next thirty-five years. Considering the escalating food security issue and future food supply, it has become necessary to increase the agriculture output throughout the globe (Garnett *et al.*, 2013). New techniques are being adopted which are mostly relying on the use of synthetic agrochemicals. The addition of these chemicals for crop protection and stimulating plant growth are associated with various undesired health and ecological site effects. Another important issue causing huge productivity loss is the presence of inorganic pollutants in the soil. In view of the toxicity of the agrochemicals and inorganic pollutants, various bio-based methods have been proposed (Swartjes *et al.*, 1999).

However, these methods are currently incapable of producing food at par with the growing demand.

In Pakistan, most of the agriculture soils are deficient in nitrogen, phosphorus and potassium (Akhtar *et al.*, 2003). In order to gain the required agriculture output, a huge amount of fertilizers are being imported. According to the Ministry of Finance, an increase of 21.1 % of the imported fertilizers was recorded in 2018 owing to the drop of 5.4 % internal manufacturing capacity. Under the situation, the demand of agriculture products is continued to increase and on the other side, fertilizer production capacity is declined (Quddus *et al.*, 2008) so innovative alternative methods should be adopted to meet the growing food demand. Furthermore, the addition of heavy metals such as Cd from various industrial and domestic activities causes severe toxicities at all trophic levels (Wieczorek- Dąbrowska *et al.*, 2013). In this connection, the application of biochar derived from the ligno-cellulosic materials has been proposed as a promising technology in order to improve agriculture productivity and reducing the impact of toxic contaminants in the soil.

Ligno-cellulosic materials derived from agricultural wastes are generated in huge quantities and serve as a renewable resource for biochar production (Loow *et al.*, 2015). It is assessed that 998 million tons of agro-wastes is produced each year (Agamuthu, 2009). Open incineration of these wastes causes atmospheric pollution and releases pollutants such as nitrous oxide, carbon monoxide, nitrogen dioxide, and smoke carbon accompanied by the production of nitric acid and ozone (Hegg *et al.*, 1987). Thus, these environmental pollutants imply a great threat to both human and ecosystem. On the other hand, these wastes contain vital nutrients i.e., N, K, and P that can improve soil fertility and crop yields. Maize crop has huge significance for countries such as Pakistan where demand of this crop is continued to grow with increasing population (Durrishahwar *et al.*, 2008). Concerns of climate change on agriculture (Gbetibouo and Hassan, 2005) and a short burst of cumulative temperature would cause infertility and reduces crop yield (McKeown *et al.*, 2005).

Biochar is carbon-enriched by-product obtained from the pyrolysis of organic biomass under high temperature and anaerobic conditions. Biochar is considered as the purest form of carbon after diamond and graphite (Lehmann *et al.*, 2002). Biochar has been investigated as biomass in pure or amended form having different useful capabilities such as soil conditioner, remediation, resistance against environmental hazards, and greenhouse gas (GHG) mitigation (IBI, 2015). The use of fossil fuels accounts for nearly 75% of CO₂ emission (Bilen *et al.*, 2008). Biochar application to soils has gained much attention as a technique to increase soil carbon sequestration while also reduces atmospheric CO₂ concentrations (Aziz *et al.*, 2020; Laird, 2008). These wastes along with others can be a better option and feedstock for producing efficient biochar which is also a magnificent strategy of waste management and waste reduction (Sugumaran and Seshadri, 2009). However, having an organized porous structural composition, biochar has the potential to store different macro and microelements in the soil for long periods. There is a magnificent need for continuous advancements in food production techniques in order to accomplish the United Nations Sustainable Development Objective to reduce famine across the globe by 2030. The application of biochar is a beneficial strategy that can boost up crop yields, and by using waste material for its production, results in the more effective use of current resources.

Biochar might prove tremendous inputs for agriculture; it could help in the rehabilitation of degraded soil, sequestering atmospheric CO₂, sustaining production, instantaneously reducing pollution, reliance on fertilizers, increase soil moisture availability, and sequester carbon (Sohi *et al.*, 2010). The use of unwanted material for biochar production is not only cost-effective but also assistive in term of primarily

including energy production and climate change mitigation (Barrow, 2012).

Another problem associated with the agriculture performance is presence of heavy metals such as cadmium in the soils. Cd is being added into the agriculture soils by means of industrial activities, wastewater irrigation, over-fertilization, and improper waste management and its dumping (Van der Ent *et al.*, 2013). It accumulates in the soil very quickly because, unlike organic pollutants, it cannot be degraded or destroyed. Cd has the tendency to bioaccumulates in plants from the polluted soil and can enter the food chain (Liu *et al.*, 2012b). Plants growth is influenced even at a very low concentration of 0.001 mg/kg soluble Cd (Kabata-Pendias *et al.*, 1993; Zhou and Qiu, 2005). Besides restrictive shoot and root growth, elevated Cd level causes oxidative stress in plants by overproducing reactive oxygen species (ROS) (Sidhu *et al.*, 2017). The ROS are extremely lethal and cause impairment to macromolecules (Li *et al.*, 2016). The application of the biochar provides essential nutrients for the plant growth and development. The aim of this research is to give a systematic characterization of biochar through EC, FT-IR, XRD and TGA. The biochar was produced under typical pyrolytic conditions at 700 °C using Maize waste as feedstock and to evaluate a strategy to reduce the bioavailable cadmium fraction in soil using wheat plants as bioremediation agent. Further, the stimulatory role of the biochar on the growth and development of the plant wheat plants was determined. It is likely that the results of the present research will address the issue of Cd toxicity in the soil and provide biochar as an alternative fertilizer for improving the yield of wheat crop.

MATERIALS AND METHODS

Collection of raw material and biochar production: The feedstock to produce biochar was collected from the Research Farm of the Cukurova University (37°00'54.31"N longitude and 35°21'21.56"E latitude and 34 m above mean sea level) in the eastern part of the Mediterranean region of Adana-Turkey. Around 500 g of the dry maize (*Zea mays* L) were placed into a stainless cylinder container (40 cm diameter, 20 cm height) which was designed to fit inside the muffle furnace (Olympic 1823HE). The cylindrical container was initially purged with nitrogen gas (10 psi) and an oxygen sensor attached to the cylinder confirmed that the oxygen in the cylinder was not more than 0.5% before it was implanted inside the furnace. The cylinder was again purged with nitrogen along with the furnace and sealed for carbonization. The regulator of the furnace was set to drive the inner biomass chamber temperature up to 700 °C and stabilized the higher temperature for 2 h before cooling to room temperature. Biochar produced in this way from the pyrolysis was mechanically crushed using Mortar and pestle and was sieved into 2mm particle size and were packed in zipper bags for further analysis.

Characterization of biochar: The pH and Electrical Conductivity of the biochar was determined in 1:5 solid to water ratio suspension using a pH meter (Eco scan, Eutech, Singapore) and conductivity meter (Eutech, Singapore) and values were indicated in *dS/m* (Zheng *et al.*, 2013). Biochar was evaluated for proximate analysis (*Moisture, Volatile Matter and Ash Contents*) by following the standard ASTM D1762–84 methods (ASTM, 2007).

$$\text{Total Ash (\%)} = (W_2 - W_C / W_1 - W_C) \times 100$$

$$\text{VM (\%)} = A - C / A - B \times 100$$

The quantitative analysis of heavy metals in biochar was determined by atomic absorption spectroscopy (AA240FS Fast Sequential Atomic Absorption Spectrophotometer). The biochar was digested with 1:3 ratio aqua regia (HCl: HNO₃) and HClO₄. The surface functional groups and crystallinity was measured by Fourier transform infrared spectroscopy (FT-IR) in the infrared region, with (Jasco FT-IR 4100) and XRD patterns were observed by (X-Pert APD Philips, Netherlands). For determination of thermal stability, Thermo gravimetric analysis (TGA) of the powdered biochar was performed out using a TG analyzer (TagongsiSDTQ600, USA) under nitrogen atmosphere. The biochar and plant samples based nutrient concentration was evaluated by inductively coupled-plasma optical emission-spectrometry (Optima 8000 ICP-OES), PerkinElmer Inc, USA. Elemental composition of biochar, plant shoots and roots were examined by CN elemental analyzer (Vario EL cube, Elementar, Germany). C and N was determined against 2 gm Aspartic Acid (Bremen- Germany C₄H₇NO₄) having 36.09% C and 10.52% N as standard. In which 0.45 to 0.6 mg of biochar was weighed and was subjected to the elemental analyzer whose combustion temperatures was respectively chosen as 900°C.

Experimental design: A pot culture trial was performed in a greenhouse of Cukurova University Adana, Turkey. Different dosage of biochar i.e., 0%, 1.5% and 3% w/w were added with air dried soil sample. The Cd was applied at the concentration of 0, 10, and 20 mg/Kg in the soil as Cd (NO₃)₂.4H₂O. The prepared 2 Kg soil was added in pots. Soil having Cd without biochar was used as control and setup was run in triplicate. The seeds of Cukurova-89 spring type bread wheat were sterilized by 3% (v/v) H₂O₂ for 10 minutes. The washing of seeds was carried out with deionized (DI) water and soaked for 10 h in an incubator. After that, 5 seeds were sown in every pot and thinned to 3 seedlings per pot. After 75 days of sowing, the plants were harvested and separated into roots and shoots and washed with diluted HCl followed by rinsed with DI water.

Plant Height, fresh and dry weight: Soon after harvesting, plant height was measured by using stainless steel scale. Fresh biomass was observed. The dry biomass was recorded at 65°C for 48 h (Mahar *et al.*, 2016). The plant tissues were pulverized and stored for further analysis.

Analysis of plant tissues for Cd uptake: 0.2 g of homogenized sample was digested in mixture having 2 mL of H₂O₂ and 5

mL of HNO₃ at 175 °C for 42 min in microwave digestion system. The volume was raised up to 20 mL by the addition of 13mL of ultrapure water. Upon cooling, the mixture was filtered. In the same way blank samples were prepared without plants and were subjected to autosampler ICP-OES, Optima 8000 (PerkinElmer Inc., USA) (Wheal *et al.*, 2011).

Root analysis through WinRHIZO root scanner: 0.5 g of plant roots was placed in a plastic tray having distilled water and set on a scanner (Epson Perfection V700, Photo Long Beach, CA, USA). Different characteristics of roots such as root surface area, root length and root volume were scanned by WinRHIZO Pro 3.10 (Regent Instruments Inc.) (Himmelbauer, 2004).

Statistical analyses: The impact of biochar on plant growth (root, shoot length and biomass) was analyzed through analysis of variance (ANOVA). The Tukey's HSD test was performed to elaborate differences between all the groups.

RESULTS

Production and characterization of biochar: The properties of the produced biochar has been shown in the Fig. 1. The pH of maize waste derived biochar was in the range of alkaline pH i.e., 8.6. In the same way, the EC of biochar was found to be 2.1 *dS/m*. indicating an optimum EC for the plants to absorb the required nutrients. In proximate analysis, moisture, volatile matter and ash content of the biochar were measured. This biochar was found to be low in nitrogen contents, however, showed higher carbon. The concentrations of various metals like Nickel, Palladium, Cadmium, Chromium, Lithium, Aluminum, Cobalt and Arsenic metals were quantitatively determined by Atomic absorption spectroscopy and represented in Table 1.

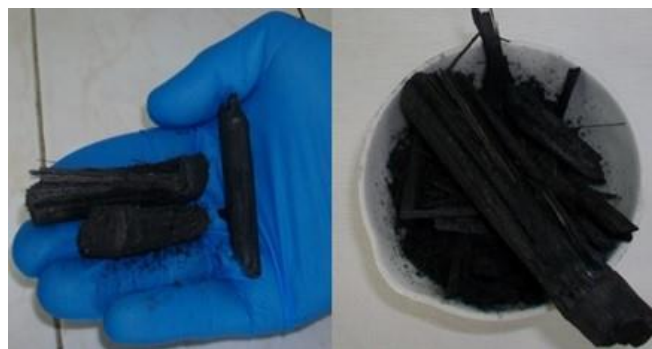


Figure 1. Production of biochar from maize at 700 °C.

X-ray Diffraction (XRD): The XRD spectra of the biochar produced from maize (*Zea mays* L.) at 700 °C has been shown in Fig. 2. All the seven prominent peaks across 2θ ranging from 23.05, 29.39, 35.96, 39.40, 43.15, 47.10, 48.49, having peak intensity [Å] 3.86, 3.03, 2.49, 2.28, 2.09, 1.92, 1.87 indicated calcite, respectively. The most prominent peak was at 3.03 confirmed the presence of 100 % calcite. It further

Table 1. Ultimate, proximate, trace metals characterization of the biochar on dry weight basis.

Trace Metals ^a					Ultimate analysis					Proximate analysis			pH	EC (dS/m)
Ni	Pd	Cd	Cr	Li	Al	Co	As	% C	% N	Moisture (%)	Volatile matter (%)	Ash (%)		
1.9	1.6	1.6	2.4	3.3	2.7	2.1	0.4	77.8	1.5	5.4	23.6	14.2	8.6	2.1

^a All values are in mg/kg

showed the chemical formula of the compound as $C_1 Ca_1 O_3$ ($CaCO_3$) showing pure hexagonal architecture. The calcite was the only material observed in the XRD spectrum of the investigated biochar sample.

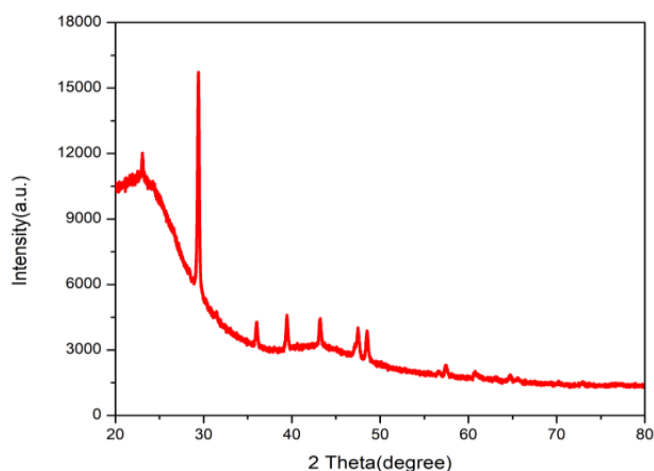


Figure 2. The X-ray diffraction spectrum of produced biochar.

Fourier transform infrared spectroscopy: The heterogeneous and complex chemical conformation of biochar was observed using FTIR spectroscopy. Dissociation and rearrangement of the chemical bonds in charred biomass resulted formation of numerous functional groups. Fig. 3 shows the FTIR spectrum in a wavelength range of 400- 4000 cm^{-1} . At 1500 cm^{-1} , the region is known as fingerprint region and the main region onward 1500 cm^{-1} is called diagnostic region.

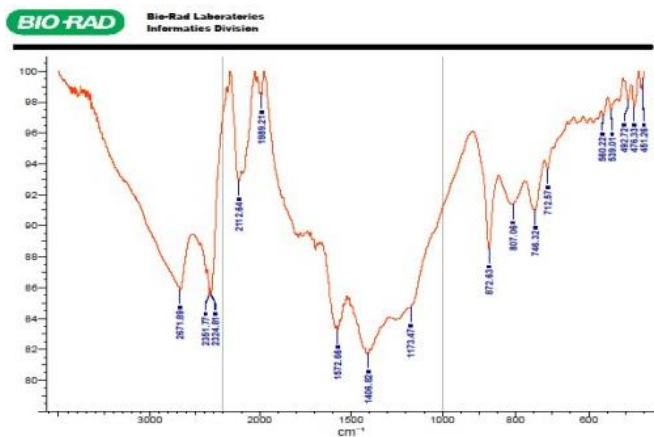


Figure 3. FT-IR spectrum of the biochar.

Some major peaks are presented in Table 2. The absorbance peak at 1572 cm^{-1} corresponding a weak aromatic ring stretch $C=C$. The peak at 1173 cm^{-1} was ascribed to alcohol $C-O$ and $C-O-C$ of cellulose. Waves at 875 to 602 cm^{-1} nearly at 872 cm^{-1} is characteristic of strong bend $C-H$ phenyl rings. A sharp band at 807 cm^{-1} could be due to aromatic $C-H$ bends on the surface of biochar which suggests the involvement of condensation during carbonization. Maize (*Zea mays* L.) derived biochar had cellulose and hemicellulose which were confirmed by the presence of oxygenated hydrocarbons. Results showed that the presence of carboxyl and hydroxyl groups in the biochar makes them suitable soil amendment for acidic soils in maintaining its pH. Peaks obtained in the region of at 2324 cm^{-1} and 2351 cm^{-1} are due to $C=C$ stretching vibrations (Saraswathi and Santhakumar, 2017).

Table 2. FT-IR spectroscopy wave number (cm^{-1}) and their respective functional groups.

Wave no. (cm^{-1})	Assignments
2671	$C-CH_3$
2112	Alkynes ($C\equiv C$ stretch)
1989	Carboxylic Acid ($C=O$)
1406	$-OH$ bending vibration and $-C-O-H$ in-plane bending vibration
500-700	$C-I$
560, 539	$C-Br$ stretches
45-492	Alkyl Halides ($C-I$)

Different types of aromatic functional groups were present in biochar which reinforces the recalcitrance property of produced biochar. Nature of these functional groups varied depending on the source of feedstock and its quality. The plant-derived biochar was dominated with $C-H$, OH group, Carboxylic Acid ($C=O$), $C-CH_3$ and Alkynes ($C\equiv C$ stretch). Several chemical interactions between biochar and environment are associated with its surface chemistry. Various functional groups like hydroxyl and carboxyl groups recommend that biochar have the efficiency to be applied as a soil amendment for boosting its capacity as a potential adsorbent (Oh *et al.*, 2012).

Inductively coupled plasma-optical emission spectrometry (ICP-OES): The elemental composition of the biochar in terms of macro and micronutrients has been summarized in Fig. 4. It was observed that, these residues were rich in calcium with a high content of potassium, magnesium, and phosphorus. Additionally, different micronutrients were also determined in which presence of Cu, followed by trace amounts of Fe, Zn, and Mn were detected.

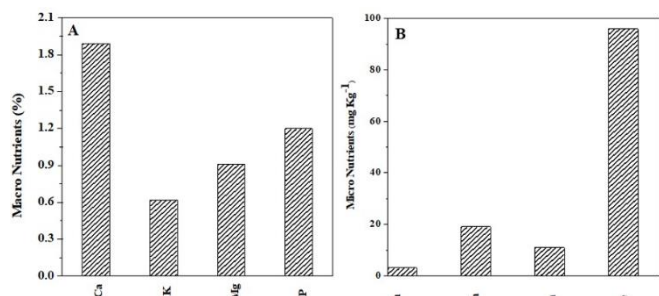


Figure 4. Biochar composition. (A) Macro nutrients, (B) Micronutrients.

Thermogravimetric (TGA) analysis of biochar: The thermogravimetric analysis of the biochar sample was performed (Pütün, 2002). It was noted that the mass of biochar was lost at four different stages from 0 to 900°C (Fig. 5). In

the very first phase, the water contents on the surface of the sample were evaporated in the range of 5.58 % at 140°C. In the 2nd stage, the internal water molecules in biochar sample were lost at almost 180 °C which consisted of 0.76 %. In addition, at 450°C, around 4.44 % volatile matter (VM) in biochar was lost by degasification. In the last peak point that continued up to 650°C. The decomposition of the inorganic matters such as Calcium Carbonate (CaCO₃) was found to be 3.32 %.

Plant height and fresh biomass of shoots: After 75 days, the plants were harvested (Fig. 6). The height of the plant was measured through measuring tape followed by observing the fresh weight; the dry weight was performed while drying at 65 °C for 48 h (Table 3). The maximum increase in height of plant shoots was 7.76% at BC 1.5%, followed by 2.16% at BC 3%, compared to the control. The fresh biomass of the wheat plant shoots was greater in all biochar treatments as compared

Table 3. Wheat plant fresh biomass, height of shoots, carbon and nitrogen value in shoots and roots in Cd-spiked soil treated with biochar.

Treatments	Pot No.	Height (cm)	Fresh biomass (g)	Shoots total C (%)	Shoots total N (%)	Roots total C (%)	Roots total N (%)
0 % BC (Control)	1	75	46.886	43.710	1.462	40.207	0.777
	2	75	37.197	43.858	1.629	36.023	1.078
	3	82	42.630	43.645	2.190	40.160	0.997
1.5 % BC	4	84	49.005	45.375	1.891	42.798	0.818
	5	82	52.036	46.310	1.644	42.328	0.813
	6	84	52.780	45.728	1.605	42.766	0.841
3 % BC	7	77	50.561	49.339	1.924	46.661	1.130
	8	81	53.968	55.542	1.416	48.729	0.961
	9	79	54.004	51.116	1.591	47.289	0.747

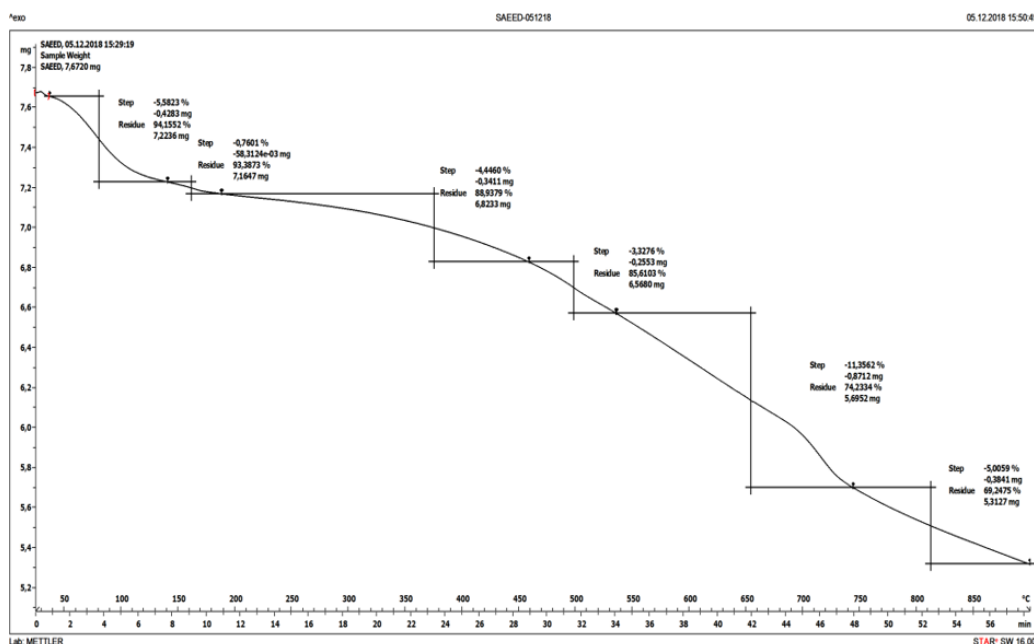


Figure 5. Thermogravimetric analysis (TGA) curve of biochar.

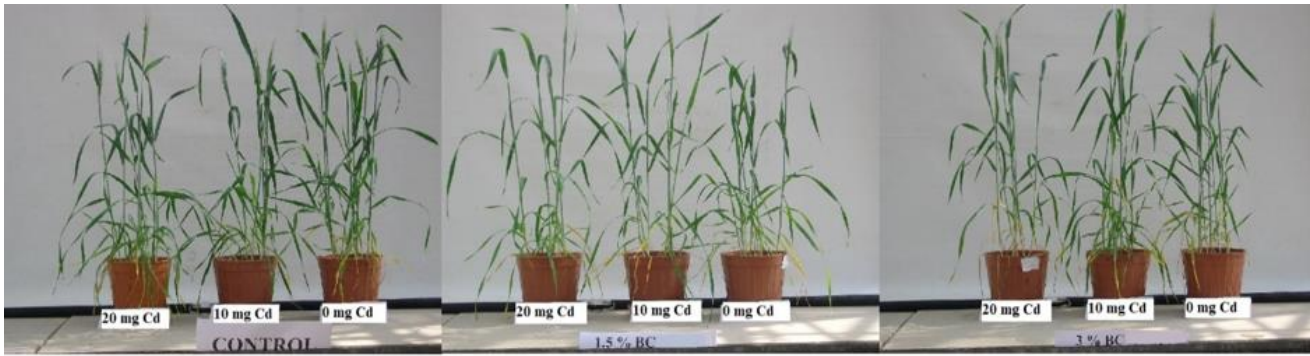


Figure 6. Pot culture experiment.

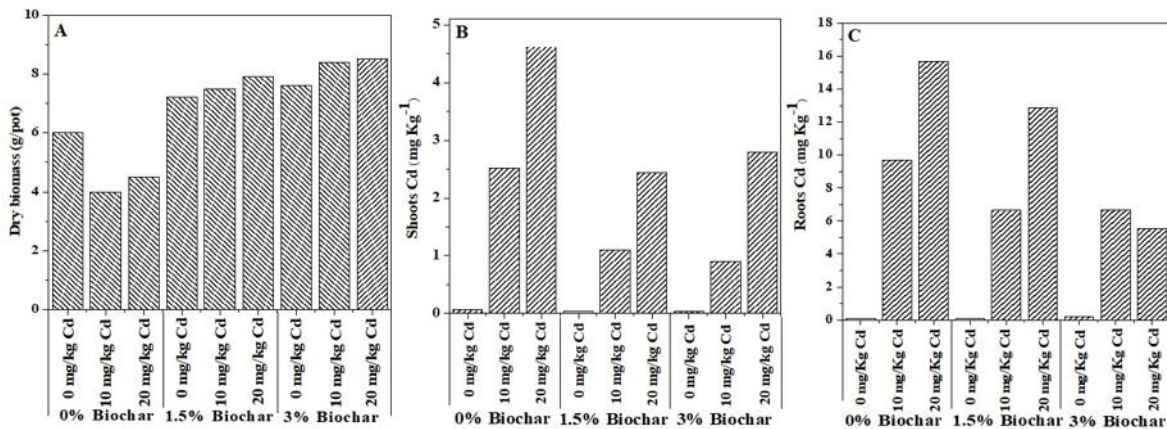


Figure 7. Effect of Biochar on (A) Dry biomass of shoots, (B) Concentration of Cd in wheat shoots, (C) Concentration of Cd in wheat roots.

to control (Table 3). The 3 % amended biochar was more effective in increasing wheat fresh biomass as compared to 1.5 % BC. The maximum growth in shoot fresh biomass at 3% BC was 25.11%, followed by 21.39% in 1.5% BC as compared to non-amended soil.

When the biochar was amended into the soil it enhanced the total carbon pool of the soil as a result wheat plant tissues had higher contents of carbon as compared to the control soil plants. Maximum carbon of shoots was observed at BC 3% which was 18.87% followed by 4.71% at BC 1.5%. In the same way, roots total carbon was analyzed and was increased by 22.59% at BC 3% and at BC 1.5% was 9.88%. It was also observed that the total nitrogen concentration of shoots and roots was not significantly affected (Table 3). **Dry biomass of wheat plant shoots:** The wheat plant dry biomass was significantly enhanced by the application of biochar (Fig. 7a). Maximum dry biomass was observed at 3% BC which was 68.97% and at 1.5% BC was 55.86%. The biochar treatments influenced the crop productivity in terms of nutrients availability and enhancing soil physical health.

Cd uptake by shoots and roots: The determined Cd ratio in wheat shoots was significantly affected within treatments. The Cd accumulation in wheat shoots was reduced by 51.1 % at 1.5 % BC followed by 48.77% at 3 % compared with

control. Additionally, the biochar decreased the Cd availability to plant in soil therefore reducing the impact on plant growth (Fig. 7b). The adding biochar minimized the Cd accumulation in the root of the wheat plant up to 23.16 % at 1.5 % BC and by 51.18% at 3% BC (Fig. 7c).

Morphological characterization of wheat roots through WinRHIZO: Wheat root length was improved by increasing the concentration of BC in contrast to control. An improvement of 23% in root length was observed at 1.5% BC and 38% in case of 3% BC. Addition of biochar enhanced 39% root surface area at BC 1.5% while it was increased by 92% at BC 3%. A similar trend was seen in root volume. This was increased by 54% at BC 1.5% and by 72% at BC 3% (Table 4).

The ANOVA revealed all significant difference among all treatments. The post-hoc comparison with Tukey test revealed that biomass of the control group significantly differ ($p < 0.001$) from the treated ones but the treated groups did not showed significant differences (Fig. 7). The group treated with 3% biochar could show insignificant difference in plant height with both control and treated subjects. Root area was not significantly different between control and 1.5% biochar treated group. The Root length was significantly different between control and 3% biochar treated group only, however,

root volume differences between 3% and 1.5% biochar treated groups were found insignificant ($p < 0.001$) (Table 4).

Table 4. Root length, root surface area and root volume of wheat plant in Cd-spiked soil.

Treatments	Pot No.	Root length (cm)	Root surface area (cm ²)	Root volume (cm ³)
0% BC (Control)	1	19,282.5	4462.3	82.2
	2	19,979.7	2885.9	33.2
	3	33,394.7	5222.0	65.0
1.5 % BC	4	32,994.1	7770.1	145.7
	5	30,160.1	5218.1	71.9
	6	26,468.6	4521.3	61.5
3% BC	7	42,812.1	10,700.6	102.9
	8	27,981.5	6378.8	97.8
	9	30,094.8	7096.8	111.2

DISCUSSION

Pakistan produces a great number of agricultural residues comprising rice husks, corn stalk, wheat husks, sugar cane residues and cotton sticks. Being an agricultural country, around 70% of the population lives in rural parts and are linked to farming (McKendry, 2002). Urban areas of the country produce nearly 20 Mt solid wastes each year and about 82.12 Mt per year of crop residue that can be easily pyrolyzed to biochar. Maize is an important crop in Pakistan which is cultivated twice in a year (autumn and spring) (Tariq and Iqbal, 2010). The production of biochar from maize biomass and its waste could potentially be a significant tool for managing waste biomass in a cost-effective and sustainable way. Furthermore, the Government of Pakistan has placed emphasis on the re-use of such wastes, as opposed to the practice of land filling.

Advantageous outcomes of biochar are linked with its physical, chemical and biological properties. Biochar mostly has elevated pH values showing alkalinity might be due to the release of minerals from the organic feedstock during the burning process. Various biochar has alkaline pH and the biochar samples in this study also recorded alkaline pH i.e 8.6, due to their Ca²⁺ and Mg²⁺ contents. The pyrolytic temperature has a significant positive effect on the pH values of biochar. The pH increases as pyrolysis temperature increase from 250°C to 800°C from a range of 6 to almost 11, due to the separation of the basic cations at elevated temperature. Uchimiya *et al.* (2012) investigated the effects of 10 different biochar on soil heavy metals concentrations produced from 5 feed stocks at two different pyrolyzing temperatures. They recorded that manures with a low or high fraction of ash or P were less effective in immobilization of heavy metals. On the other hand, biochar pyrolyzed at 700 °C was significantly effective, which might be attributed to transformations in the biomass, comprising the removal of

different nitrogen-containing heteroaromatic and leachable aliphatic functional groups.

Biochar is an emerging soil amendment rich in carbon (more than 70%) and contains vital nutrients for the growth of plants. Furthermore, its amendment in soil modifies soil agriculture properties and promotes growth and colonization of the soil microbiota. In this study; the effect of biochar amendments increased the wheat growth. However, the doubling of biochar ratio did not proportionally enhance the fresh and dry biomass and the height of plants. Amendment of biochar increased fresh biomass by 21% (BC 1.5%) and 25% (BC 3%). Also, plant dry biomass was enhanced by 55% (BC 1.5%) and 68% (BC 3%). Matovic (2010) assessed that the optimal addition of biochar in agriculture soil ranged from 1% to 5% which is similar to our results.

In pot culture experiment, the macronutrient analysis of biochar was carried out for sustainable increased crop yields by use of biochar. Macro-nutrients (Ca, P, K, Mg) and Micro-nutrients (Fe, Mn, Cu, Zn) concentrations in biochar were enough in maize derived biochar. Maximum Ca was investigated as 1.89% along with K 0.27 %, Mg 0.06 and P 0.01 %. In the same way, micronutrients were also found in the produced biochar in trace amounts. The micro and macronutrients enhance the overall plant yield and plant growth. The amendment of biochar in the soil also reduces the application of chemical fertilizer. The biochar was proved to be more advantageous as it remains in the soil for longer periods as compared to chemical fertilizers which replenish after a year.

The findings in the greenhouse experiment explain that in terms of plant fresh and dry biomass, plant height, Cd immobilization in shoots and roots and total carbon both at 1.5 and 3% BC treatments is optimal. Because both amendments notably enhanced the wheat biomass, that might be ascribed in reduction of Cd toxicity and improving nutrients. Similar results were recorded by Hossain *et al.* (2010). Who analyzed the impact of sludge derived biochar upon the growth of *Lycopersicon esculentum*. The adding of 10 Mg/ha biochar enhanced shoot dry biomass from 61 to 73 g/plant, which is the 64% greater yield as compared to control. In the same way, 1 % addition of wood chips and *Eucalyptus* derived biochar increased the spring onion biomass than control (Luo *et al.*, 2014). We can assume that Cd immobilization in the BC 1.5% and 3% treatments was carried out both by precipitation with mineral ash and by pH changes. Therefore, Ash content in the produced biochar of this study ranged from 2.5 to 55%, which must be enriched by mineral salts of K, Ca, Mg, C and P. so cadmium can precipitate as carbonate salts and insoluble phosphate (Uchimiya *et al.*, 2012).

Temperature and availability of feedstock are the most influential factors in the disintegration of herbaceous and woody biomass to manufacture biochar (Zhao *et al.*, 2013). Hemicellulose is easily degraded among three major

components, with thorough combustion imitating at 330 °C (Buss *et al.*, 2015). The major fraction of cellulose degradation happens at a temperature above 427 °C, though burning might occur at lower temperatures, producing much volatile matter as carbon-hydrogen and carbon-oxygen linkages are broken (Buss *et al.*, 2015). Among all three key constituents, lignin is recalcitrant to degradation, which is only possible when pyrolyzing temperature exceeds 607 °C. which is due to lignin's configuration comprising of numerous ether bonds and functional groups such as methoxy and hydroxyl (Askeland *et al.*, 2019). So, pyrolysis temperature increases pH, carbon content and porosity as noticed in the above investigated biochar. Biochar burned at high temperature has numerous cracks and pores on the surface, indicating an increased surface area of the produced biochar, which provide better adsorption sites, water retention and space for nutrients.

Different research works have investigated that application of biochar has magnificent potential in immobilization of metal, which minimizes the bioavailability and phytotoxicology of toxic metals. Baronti *et al.*(2010). assessed the efficacy of applying biochar to ameliorate the metal toxicity in the mine tailings. They amended biochar derived from orchard prune remains at four different rates (0%, 1%, 5% and 10%). They observed that water holding capacity, pH, and CEC increased while increasing the rate of biochar and the availability of metals such as Cd, Zn and Pb decreased, while Cd had the highest reduction. Xu *et al.* (2016) treated the Cd by applying the cotton stalk derived biochar and explored the Cd up taking capacity by cabbage. The result showed that used biochar had the potential to reduce the bioavailability of Cd via co-precipitation or adsorption. Méndez *et al.*(2012) observed the impacts of sewage sludge derived biochar upon solubility and bioavailability of heavy metals in a Mediterranean agriculture soil. The different factors of biochar decreased Zn, Ni, Pb, and Cd as compared to sewage sludge derived biochar. Our findings in the performed research also matched with these previous studies and explored that processed biochar reduced Cd in wheat shoots by 51% at BC 1.5% and 48% at BC 3%. Growth of wheat plant in biochar amended soil also was increased.

The mobility and availability of heavy metals in soil depend on the organic source, pH, Fe/Al oxides and clay minerals. Organic source offers a novel eco-friendly opportunity to reduce metal accumulation in eatable parts of plants. Adsorption, precipitation and complexation are the key pathways in metal immobilization process by organic amendment (Shuman, 1999). Organic biomass has different reactive groups such as carboxyl and hydroxyl that react with soluble cadmium to form stable complexes (Hamid *et al.*, 2018). Biochar application to soil leads to several interactions mainly with soil matrix, soil microbes, and plant roots (Lehmann and Joseph, 2009).

Conclusion: In present work, biochar was produced from the waste of *Zea mays* for its use as plant growth promotor and cadmium removal. Our results suggested that the biochar was very effective in cadmium immobilization up to 51% and effectively enhanced the growth of the wheat plants. At 3 % biochar amendment, plant root length, root surface area, root volume and total carbon off shoots were significantly improved as compared to the control. In conclusion, application of the biochar could be very effective for heavy metal remediation and for the improvement of agriculture productivity.

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REFERENCES

- Agamuthu, P. 2009. Challenges and opportunities in agro-waste management: An Asian perspective, Inaugural meeting of first regional 3R forum in Asia. pp.11-12.
- Akhtar, M., M. Ashraf and M.E. Akhtar. 2003. Sugarcane yield gap analysis: Future options for Pakistan. *Sci. Tech. and Devel.*1:38-48.
- Angin, D. 2013. Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake. *Bioresour. Technol.* 128:593-597.
- Askeland, M., B. Clarke and J. Paz-Ferreiro. 2019. Comparative characterization of biochars produced at three selected pyrolysis temperatures from common woody and herbaceous waste streams. *Peer J.* 7:e6784.
- Aziz, S., L. Yaseen, A. Jamal, U. Farooq, Z. Qureshi, I. Tauseef, S.K. Haleem, and M.I. Ali. 2020. Fabrication of Biochar from Organic Wastes and its Effect on Wheat Growth and Soil Microflora. *Pol. J. Environ. Stud.* 29(2):1069-1076.
- ASTM, A. 2007. Book of standards volume 15.01: refractories, activated carbon. Advanced ceramics. American Society for Testing Materials, West Conshohocken.
- Baronti, S., G. Alberti, G. Delle Vedove, F. Di Gennaro, G. Fellet, L. Genesio, F. Miglietta, A. Peressotti and F.P. Vaccari. 2010. The biochar option to improve plant yields: first results from some field and pot experiments in Italy. *Ital. J. Agron.*5:3-12.
- Barrow, C. 2012. Biochar: potential for countering land degradation and for improving agriculture. *Appl. Geogr.* 34:21-28.
- Bilen, K., O. Ozyurt, K. Bakırcı, S. Karlı, S. Erdogan, M. Yılmaz and O. Comaklı. 2008. Energy production, consumption, and environmental pollution for

- sustainable development: A case study in Turkey. *Renew. Sust. Energ.* 12:1529-1561.
- Buss, W., O. Mašek, M. Graham and D. Wüst. 2015. Inherent organic compounds in biochar—their content, composition and potential toxic effects. *J. Environ. Manag.* 156:150-157.
- Cantrell, K.B., P.G. Hunt, M. Uchimiya, J.M. Novak and K.S. Ro. 2012. Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. *Bioresour. Technol.* 107:419-428.
- Durrishahwar, H., S.M.A. Shah, I.A. Khalil and F. Ali. 2008. Recurrent selection for yield and yield associated traits under leaf blight (*Helminthosporium maydis*) stress in maize. *Sarhad J. Agric.* 24:599-605.
- Dwivedi, S., Q. Saquib Q, A.A. Al-Khedhairi and J. Musarrat. 2016. Understanding the role of nanomaterials in agriculture. *Microbial Inoculants in Sustainable Agricultural Productivity*. Springer. 271-288.
- Gao, W., X. Feng, A. Pei, Y. Gu, J. Li and J. Wang. 2013. Seawater-driven magnesium based Janus micromotors for environmental remediation. *Nanoscale* 5: 4696-4700.
- Garnett, T., M.C. Appleby, A. Balmford, I.J. Bateman, T.G. Benton, P. Bloomer, B. Burlingame, M. Dawkins, L. Dolan and D. Fraser. 2013. Sustainable Intensification in Agriculture: Premises and Policies. *Sci.* 341:33-34.
- Gbetibouo, G.A. and R. Hassan. 2005. Measuring the economic impact of climate change on major South African field crops: a Ricardian approach. *Glob. Planet. Change.* 47:143-152.
- Gładki, J. 2017. Biochar as a chance for sustainable development: On the Basis of the Work and Own Research of FLUID, 2nd Ed. *Apla Sp. J., Sędziszów, Poland.*
- Glaser, B., J. Lehmann and W. Zech. 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal—a review. *Biol. Fert. Soils.* 35:219-230.
- Hamid, Y., L. Tang, X. Wang, B. Hussain, M. Yaseen, M.Z. Aziz and X. Yang. 2018. Immobilization of cadmium and lead in contaminated paddy field using inorganic and organic additives. *Sci. Rep.* 8:7839.
- Hegg, D.A., L.F. Radke, P.V. Hobbs, C.A. Brock and P.J. Riggan. 1987. Nitrogen and sulfur emissions from the burning of forest products near large urban areas. *J. Geophys. Res.-Atmos.* 92:14701-14709.
- Himmelbauer, M.L. 2004. Estimating length, average diameter and surface area of roots using two different image analyses systems. *Plant Soil.* 260:111-120.
- Hossain, M.A., M. Hasanuzzaman and M. Fujita. 2010. Up-regulation of antioxidant and glyoxalase systems by exogenous glycinebetaine and proline in mung bean confer tolerance to cadmium stress. *Physiol. Mol. Biol. Pla.* 16:259-272.
- Hofstra, N and L.C. Vermeulen. 2016. Impacts of population growth, urbanization and sanitation changes on global human *Cryptosporidium* emissions to surface water. *Int. J. Hyg. Environ. Health.* 219:599-605.
- Kabata-Pendias A, Motowiecka-Terelak T, Piotrowska M, Terelak H, Witek T 1993. Assessment of contamination level of soil and plants with heavy metals and sulphur, IUNG Pulawy Publisher. 53:1-20
- Laird, D.A. 2008. The charcoal vision: a win-win-win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. *Agron. J.* 100:178-181.
- Lal, R. 2006. Enhancing crop yields in the developing countries through restoration of the soil organic carbon pool in agricultural lands. *Land Degrad. Dev.* 17:197-209.
- Lal, R. 2009. Soil degradation as a reason for inadequate human nutrition. *Food Sec.* 1:45-57.
- Lee, Y., J. Park, C. Ryu, K.S. Gang, W. Yang, Y.K. Park, J. Jung and S. Hyun. 2013. Comparison of biochar properties from biomass residues produced by slow pyrolysis at 500 C. *Bioresour. Technol.* 148:196-201.
- Lehmann, J., J.R. Da Silva, P. J, M. Rondon, M.D.S. Cravo, J. Greenwood, T. Nehls, C. Steiner and B. Glaser. 2002. Slash-and-char-a feasible alternative for soil fertility management in the central Amazon. *Proc. 17th World Congress of Soil Science, Thailand.* pp.1-12.
- Lehmann, J. and S. Joseph. 2009. Biochar for environmental management. *Sci. Technol.* 1:449.
- Li, R., J.J. Wang, B. Zhou, M.K. Awasthi, A. Ali, Z. Zhang, L.A. Gaston, A.H. Lahori and A. Mahar. 2016. Enhancing phosphate adsorption by Mg/Al layered double hydroxide functionalized biochar with different Mg/Al ratios. *Sci. Total Environ.* 559:121-129.
- Liu, M., R. Liu and W. Chen. 2013. Graphene wrapped Cu₂O nanocubes: non-enzymatic electrochemical sensors for the detection of glucose and hydrogen peroxide with enhanced stability. *Biosens. Bioelectron.* 45:206-212.
- Loow, Y.L., T.Y. Wu, K.A. Tan, Y.S. Lim, L.F. Siow, M.J. Jahim, A.W. Mohammad and W.H. Teoh. 2015. Recent advances in the application of inorganic salt pretreatment for transforming lignocellulosic biomass into reducing sugars. *J. Agr. Food Chem.* 63:8349-8363.
- Luo, Y., Y. Jiao, X. Zhao, G.T. Li, L.X. Zhao and H.B. Meng. 2014. Improvement to maize growth caused by biochars derived from six feedstocks prepared at three different temperatures. *J. Integr. Agr.* 13:533-540.
- Mahar, A., P. Wang, A. Ali, Z. Guo, M.K. Awasthi, A.H. Lahori, Q. Wang, F. Shen, R. Li and Z. Zhang. 2016. Impact of CaO, fly ash, sulfur and Na₂S on the (im) mobilization and phytoavailability of Cd, Cu and Pb in contaminated soil. *Ecotox. Environ. Safe.* 134:116-123.
- Marris, E. 2006. Putting the carbon back: Black is the new green. *Nature Publishing Group.* 442:624-6.

- McKendry, P. 2002. Energy production from biomass (part 1): overview of biomass. *Bioresour. Technol.* 83:37-46.
- McKeown, A., J. Warland and M.R. McDonald. 2005. Long-term marketable yields of horticultural crops in southern Ontario in relation to seasonal climate. *Can. J. Plant Sci.* 85:431-438.
- Méndez, A., A. Gómez, J. Paz-Ferreiro and G. Gascó. 2012. Effects of sewage sludge biochar on plant metal availability after application to a Mediterranean soil. *Chemosphere.* 89:1354-1359.
- Oh, T.K., B. Choi, Y. Shinogi and J. Chikushi. 2012. Effect of pH conditions on actual and apparent fluoride adsorption by biochar in aqueous phase. *Water Air Soil Poll.* 223:3729-3738.
- Püttin, A.E. 2002. Biomass to bio-oil via fast pyrolysis of cotton straw and stalk. *Energ. Source.* 24:275-285.
- Quddus, M.A, M.W.Siddiqi, M.M.Riaz. 2008. the demand for nitrogen, phosphorus and potash fertilizer nutrient in pakistan. *Pakistan Econ. Soc. Rev.*46:101-116.
- Robertson, G.P. and S.M. Swinton. 2005. Reconciling agricultural productivity and environmental integrity: a grand challenge for agriculture. *Front. Ecol. Environ.* 3:38-46.
- Sanchez-Martin, M., M. Sanchez-Camazano and L. Lorenzo. 2000. Cadmium and lead contents in suburban and urban soils from two medium-sized cities of Spain: influence of traffic intensity. *Bull. Environ. Contam. Toxicol.* 64: 250-257 .
- Saraswathi, V.S. and K. Santhakumar. 2017. Green synthesis of silver nanoparticles mediated using *lagerstroemia speciosa* and photocatalytic activity against azo dye. *Mech. Mat. Sci. Eng.* 9(1): 259-263
- Shuman, L.M. 1999. Organic waste amendments effect on zinc fractions of two soils. *J. Environ. Qual.* 28:1442-1447.
- Sidhu, G.P.S., H.P. Singh, D.R. Batish and R.K. Kohli. 2017. Appraising the role of environment friendly chelants in alleviating lead by *Coronopus didymus* from Pb-contaminated soils. *Chemosphere* 182:129-136.
- Sohi, S.P., E. Krull, E. Lopez-Capel and R. Bol. 2010. A review of biochar and its use and function in soil. *Adv. Agron. Elsevier*, pp. 47-82.
- Sugumaran, P. and S. Seshadri. 2009. Evaluation of selected biomass for charcoal production. *J. Sci. Ind. Res.* 86:719-723.
- Swartjes, F.A. 1999. Risk-based assessment of soil and groundwater quality in the netherlands. *Standards and remediation urgency. Risk Analysis* 19:1235-1248.
- Tao, F., M. Yokozawa, Y. Hayashi and E. Lin. 2003. Changes in agricultural water demands and soil moisture in China over the last half-century and their effects on agricultural production. *Agr. Forest Meteorol.* 118:251-261.
- Tariq, M. and H. Iqbal. 2010. Maize in Pakistan-an overview. *Kasetsart J. Nat. Sci.* 44:757-763
- Uchimiya, M., D.I. Bannon and L.H. Wartelle. 2012. Retention of heavy metals by carboxyl functional groups of biochars in small arms range soil. *J. Agr. Food Chem.* 60:1798-1809.
- Wheal, M.S., T.O. Fowles and L.T. Palmer. 2011. A cost-effective acid digestion method using closed polypropylene tubes for inductively coupled plasma optical emission spectrometry (ICP-OES) analysis of plant essential elements. *Anal. Methods* 3:2854-2863.
- Wieczorek-Dąbrowska, M., A. T. Marciniak, B. Pilarczyk, and A. Balicka-Ramisz. 2013. Roe and red deer as bioindicators of heavy metals contamination in north-western Poland. *J. Chem. Ecol.* 29:100-110.
- Woods, W.I., N.P. Falcão and W.G. Teixeira. 2006. Biochar trials aim to enrich soil for smallholders. *Nature.* 442:624-626
- Wu, T.Y., S.L. Lim, P.N. Lim and K.P.Y. Shak. 2014. Biotransformation of biodegradable solid wastes into organic fertilizers using composting or/and vermicomposting. 17th Conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction 39:1579-1584.
- Xie, T., K.R. Reddy, C. Wang, E. Yargicoglu and K. Spokas. 2015. Characteristics and applications of biochar for environmental remediation: a review. *Crit. Rev. Env. Sci. Tec.* 45:939-969.
- Xu, P., C.X. Sun, X.Z. Ye, W.D. Xiao, Q. Zhang and Q. Wang. 2016. The effect of biochar and crop straws on heavy metal bioavailability and plant accumulation in a Cd and Pb polluted soil. *Ecotox. Environ. Saf.* 132:94-100.
- Zhao, B., S. Wang, X. Dong, J. Wang, L. Duan, X. Fu, J. Hao and J. Fu. 2013. Environmental effects of the recent emission changes in China: implications for particulate matter pollution and soil acidification. *Environ. Res.* 8:024031.
- Zhou, W. and B. Qiu. 2005. Effects of cadmium hyperaccumulation on physiological characteristics of *Sedum alfredii* Hance (*Crassulaceae*). *Plant Sci.* 169:737-745.

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