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Original article

# The effects of biochars produced in different pyrolsis temperatures from agricultural wastes on cadmium uptake of tobacco plant

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ABSTRACT

Abiotic stresses caused by cadmium (Cd) contamination in soil retard plant growth and decline the quality of food. Amendment of biochar was reported effective in reduction of mobility, plant uptake and toxicity of Cd in plants. The aim of this study was to investigate the effect of biochar applications produced from corn cob and rice husk at three different pyrolysis temperatures (400, 500 and 600 °C) on Cd uptake of tobacco plants. The results showed that the shoot Cd concentration and content of tobacco plants significantly increased with the application of Cd in increasing doses. The results showed that increasing Cd doses caused significant increase ($P < 0.01$) in shoot Cd concentration and content of the tobacco plant at three different pyrolysis temperatures of both corn cob and rice husk biochars. The concentration of Cd was 0.48 mg $kg^{-1}$ in Cd0 dose of corn cob biochar produced at 500 °C and increased to 61.6 mg $kg^{-1}$ at Cd5, while Cd concentration increased to 72.3 mg $kg^{-1}$ with rice husk biochar. Despite the increase in Cd concentrations and content, shoot Cd concentrations and contents were significantly ($P < 0.01$) reduced with the treatments of corn cob and rice husk biochars produced at different pyrolysis temperatures. The Cd concentration at Cd5 dose in the absence of biochar addition was 90.5 mg $kg^{-1}$, while Cd concentration at Cd5 dose in 400, 500 and 600 °C treatments of corn cob biochar was reduced to 66.5, 61.6 and 67.3 mg $kg^{-1}$ respectively, and to 77.0, 72.3 and 70.2 mg $kg^{-1}$ in rice husk biochar. The results also revealed that corn cob biochar treatments were more effective in reducing Cd uptake of tobacco plants compared to rice husk biochar. Higher specific surface area of corncob biochar compared to rice husk biochar caused to the difference between two biochar sources on Cd uptake of tobacco plants.

## 1. Introduction

Cadmium (Cd) has toxic effects on living organisms and is considered as an important pollutants in the ecosystem (Di Toppi and Gabbrielli, 1999; Haider et al., 2021). Despite the low natural concentration in soil, Cd may be introduced to soil from various sources. The Cd reaches to soil through natural sources (parent material) or anthropogenic activities such as industry and phosphorus fertilizers (Cheng et al., 2014). The uptake of Cd by plants is higher compared to other metals due to the higher water solubility and mobility in water. The Cd causes many physiological changes by altering the nitrogen and carbohydrate metabolism in plants. The Cd inactivates the enzymes in -SH groups of proteins, leads to the closure of stomas, reduction of water loss by transpiration and deterioration of chlorophyll biosynthesis (Sheoran et al., 1990).

Carbon-rich materials obtained by heating a variety of biomass such as wood, animal manure and leaves in an oxygen free or limited environment are called biochars (Lehmann and Joseph, 2012). Biochar has superior characteristics compared to the other organic materials due to the high charge density (Liang et al., 2006; Xiong et al., 2021), nutrient retention capacity (Lehmann et al., 2003) and high resistance to microbial degradation (Cheng et al., 2006) due to the specific chemical (Baldock and Smernik, 2002) and colloidal structure (Lehmann et al., 2005). Positive responses of biochar applications despite the significant loss of nutrients during pyrolysis process, were attributed to the neutralization of toxins (Wardle et al., 1998), especially to improvement of physical properties of soils such as water retention (Günal et al., 2018) development of a protection mechanism against heavy metal pollution (Khan et al., 2013) and reduction of soil compaction due to low bulk density (Chen et al., 2008). Physical and chemical characteristics of

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biochars significantly vary depending on the properties of raw material and conditions of the pyrolysis environment. The structure of porosity, nutrient content, pH and phenolic content of biochars depend on the type of raw material and the duration and temperature of pyrolysis process (Novak et al., 2009; Xu et al., 2021). The increase in pyrolysis temperature causes a decrease in components of –OH and –CH, an increase in C = C moieties and also amine-N transfers to the pyridine-N compounds (Chan and Xu, 2012). Adsorption of a biochar material is affected by the crystallinity of structure which becomes highly porous as temperature of pyrolysis increases (Lua et al., 2004). Specific surface area of biochars increased from 10 $m^2\ g^{-1}$ to 400 $m^2\ g^{-1}$ by increasing the pyrolysis temperature from below 400 °C to 550–600 °C (Lehmann, 2007). Sun et al. (2011) reported that specific surface area of biochar produced from chicken manure was higher compared to biochar produced from wheat straw at the same temperature (400 °C). The specific surface area of biochars produced at higher temperatures are in general higher and their aromaticity is greater compared to those produced at lower temperatures (Ahmad et al., 2012; Rodriguez et al., 2020). The surface area of well carbonized biochars produced at 500–700 °C from wheat straw were reported as 300 $m^2\ g^{-1}$, while the surface area of biochars produced at 300–400 °C was 200 $m^2\ g^{-1}$ due to the inadequate carbonization (Chun et al., 2004).

The biochar improves physical chemical and biological properties of soils and also serves as the protection mechanism against heavy metal pollution of soils. Biochars have also been reported to have positive effects in preventing heavy metal stress of soils (Khan et al., 2013; Erdem et al., 2017a,b). Zhou et al. (2008) reported that the biochar produced from cotton stalk was capable of holding higher Cd in soils contaminated with Cd. Biochar in soil decreases the biological effects of Cd by increasing the physical stability in soil (Cui et al., 2004), constraining the mobility of Cd (Hua et al., 2009) and changing the morphological structure of Cd (Zhang et al., 2014). Since biochar obtained with low cost, has a large number of potential uses and benefits in the environment, the use of biochars as adsorbents recently attracted a remarkable attention. Several studies reported that biochars produced from agricultural wastes can successfully bind heavy metals and organic pollutants in water and soil (Chen et al., 2008; Kasozi et al., 2010; Shakoor et al., 2020).

Tobacco plants can accumulate high Cd concentration in leaves, in which the Cd concentration shows a wide variation depending on soil and climate condition, characteristics of tobacco genotypes, and other influential factors (Lugon-Moulin et al., 2004). Despite the continuing warning on hazardous impacts of cigarette, the number of smokers steadily increases in most part of the world, and approximately one third of adults continue smoking (Anonymous, 2019). One of the most common mechanisms of Cd uptake by humans is the tobacco smoke, therefore, information on Cd uptake by the different tobacco cultivars under several Cd concentrations are important (Vasiliadou and Dordas, 2009). This study was carried out to determine the effect of biochars produced in different pyrolysis temperatures on Cd uptake of tobacco plants grown under increasing doses of Cd treatments.

## 2. Material and methods

### 2.1. Plant and soil material

The experiment was conducted using Xanthi/81 tobacco genotype in the greenhouses of Tokat Gaziosmanpasa University Tokat/Turkey. The Xanthi/81 is a medium-late flowering genotype with an average plant height of 65 to 105 cm, and the number of leaves for each plant is between 30 and 32. The fine textured genotype is highly fragrant, has 10–12% sugar content and the nicotine ratio is around 2.80% (Kinay, 2014). The experimental soil was in clayey-loam texture, high in $CaCO_3$ content (22.1%), slightly alkaline pH (7.93) and low in organic matter content (1.17%). The DTPA extractable Zn, Fe, Mn, Cu and Cd concentrations were 0.30, 11.2, 6.42, 2.66 and 0.004 mg $kg^{-1}$, respectively. In the experiment, biochars produced at different temperatures from two different agricultural wastes (corn cob and rice husk) were used.

### 2.2. Production and characterization of biochars

Ground corn cob and rice husk were pyrolyzed at 400, 500 and 600 °C in an ingeniously developed reactor. The heating rate biomass was approximately 10 °C $min^{-1}$ (slow pyrolysis). The biochars were kept in the pyrolysis unit until disappearance of pyrolysis gas for about 4 to 6 h, and the biochars were held in the unit till cooling to the room temperature. Both biochar materials were ground to 2 mm before mixing to soil (Zheng et al., 2013). The pH of biochars were determined in 1(biochar):5(water) suspension using a pH meter (Zheng et al., 2013). Total carbon and nitrogen concentrations were measured using a CHN analyzer (Leco, USA). Total Cd, Fe, Zn, Mn and Cu concentrations of biochar samples were measured by an inductively coupled plasma optical emission spectrometer (ICP-OES) (Varian Vista). Specific surface area was determined according to ethylene glycol mono ethylene ether (EGME) method (Cerato and Lutenegger, 2002). Total Cd concentration of biochars used in the experiment were < 0.002 mg $kg^{-1}$, pH values ranged from 8.79 to 10.2 in corn cob, and 9.21 to 11.2 in rice husk. The C/N ratio increased with the increasing temperature and the C/N ratios of corn cob biochar produced at 400, 500 and 600 °C were 276, 307 and 342 respectively, while the C/N ratio of rice husk biochars was 125, 136 and 202, respectively. The increase in temperature caused a significant increase in specific surface area which were 235, 297 and 337 $m^2\ g^{-1}$ for corn cob biochar and 170, 212 and 234 $m^2\ g^{-1}$ for rice husk biochar (Table 1).

### 2.3. Greenhouse experiment

Tobacco seedlings were carefully transferred into the plastic pots (220 × 180 mm, 3-liter volume) with 2.75 kg clay loam soil. The soil, prior to the potting was homogenously mixed with basal treatments of N 250 mg $kg^{-1}$ soil as $Ca(NO_3)_2{\cdot}4H_2O$, P 100 mg $kg^{-1}$ soil as $KH_2PO_4$ and Fe 2.0 mg $kg^{-1}$ soil as Fe-EDTA and Zn 2.0 mg $kg^{-1}$ soil as $ZnSO_4{\cdot}7H_2O$ Cadmium treatments were 0, 2.5 and 5.0 mg Cd $kg^{-1}$ soil in the form of $3(CdSO_4).8H_2O$ with three replicates. According to the randomized plot design, the corn cob and rice husk biochars produced at different temperatures were applied at a rate of 1% (w/w) and mixed homogeneously with soil during the establishment of the experiment. Tobacco plants were harvested in the 61 days when the Cd toxicity symptoms were observed. Harvested tobacco plants were dried at 70 °C in an oven, and dry weights (DW) were recorded.

### 2.4. Plant analyses

The digestion of harvested plants was performed in a microwave oven using 2 ml of 35% $H_2O_2$ and 5 ml of 65% $HNO_3$. The Cd, Fe, Zn, Cu and Mn concentrations in the extracts of digestions were analyzed using an ICP-OES (Varian Vista) (Bataglia et al., 1983). The shoot dry weight was multiplied by the concentration in the extract to determine the concentration of each metal. Reference leaf samples of National Institute of Standards and Technology (Gaithersburg, MD, USA) were used to validate the measurements of the metals. The Cd contents of the shoot was calculated by multiplying the shoot dry weights with Cd concentrations.

**Table 1**
Physical and chemical properties of biochar materials produced at different temperatures.

| Biochar type | Pyrolysis temp. (°C) | pH | C/N ratio | Specific surface area ($m^2$ $g^{-1}$) | Cd | Zn | Fe |
|---|---|---|---|---|---|---|---|
| | | | | | Concentration (mg $kg^{-1}$) | | |
| Corncob (CB) | 400 | 8.79 | 276 | 235 | <0.002 | 91.8 | 1120 |
| | 500 | 9.21 | 307 | 297 | <0.002 | 93.6 | 1004 |
| | 600 | 10.2 | 342 | 337 | <0.002 | 100.3 | 990 |
| Rice husk (RB) | 400 | 9.21 | 125 | 170 | <0.002 | 33.1 | 1075 |
| | 500 | 10.2 | 136 | 212 | <0.002 | 38.0 | 1231 |
| | 600 | 11.2 | 202 | 234 | <0.002 | 41.3 | 1516 |

### *2.5. Statistical analysis*

Significance of treatment means was assessed using the variance techniques. The data were subjected to variance analysis based on randomized plot design with MSTAT-C statistical software. The means of treatments were compared with Duncan's homogeneity test.

## 3. Results and discussion

### *3.1. Shoot dry matter, shoot Cd concentration and content*

Biochar type, pyrolysis temperature and Cd treatments had statistically significant ($P < 0.01$) effect on shoot dry matter yield of tobacco plant (Table 2, 3 and 4). Increasing Cd doses resulted in statistically significant reductions in shoot dry matter yield of tobacco plants at all temperature applications of both corn cob and rice husk biochars (Table 2 and 3). Shoot dry matter yield in Cd 0 mg $kg^{-1}$ (Cd0) treatment of corn cob biochar produced at 500 °C (CB500) was 6.31 g $plant^{-1}$ and decreased to 3.72 g $plant^{-1}$ (69.6% reduction) with 5 mg $kg^{-1}$ (Cd5) treatment. The decrease in shoot dry matter yield due to increased Cd doses from Cd0 (5.21 g $plant^{-1}$) to Cd5 (4.70 g $plant^{-1}$) was 10.8% with rice husk biochar produced at 500 °C (RB500). Similar trends have been observed for biochars produced at 600 °C. Shoot dry matter yield in Cd0 dose (4.99 g $plant^{-1}$) of CB treatment reduced to 2.99 g $plant^{-1}$ (68.6% reduction) with Cd5 dose. Similarly, shoot dry matter yield in Cd0 dose (5.94 g $plant^{-1}$) of RB treatment reduced to 3.67 g of $plant^{-1}$ (61.8% reduction) with Cd5 dose. Shoot dry matter yield in CB400 treatment increased with increasing Cd doses from Cd0 to Cd5, while shoot dry matter yield significantly decreased (42.3%) in RB400 treatment. The results revealed that both CB and RB resulted in greater shoot dry matter yield losses with the increasing Cd doses in 600 °C biochar treatments compared to other temperatures (400 and 500 °C). The decrease in shoot dry matter yields can be attributed to the high C/N ratio and specific surface areas of both biochar types produced at 600 °C (Table 1). The decrease in yield resulting from biochar treatments was attributed to the reduced availability of nutrients in soil due to the negative charge and high ion exchange capacity (Zhang et al., 2009), large porosity (Chen and Yuan, 2011) and high adsorption ability of biochar materials (Braida et al., 2003). The increasing biochar doses can cause a decrease in yield due to burning effect on plant roots. Subedi et al. (2016) investigated the effects of biochars produced from poultry manure (400 and 600 °C), pork manure (400 and 600 °C) and kiwi tree pruning wastes (1000 °C) on rye growth in two different soils with silty and sandy textures. Biochar produced from animal manure at low temperature (400 °C) significantly increased both shoot and root dry matter yields. However, biochars produced from animal manure and wood at 600 °C had no effect on shoot and root dry matter yields.

The effect of biochar type, temperature and Cd doses on the shoot Cd concentration and content was important at $P < 0.01$ level (Table 4). The increasing Cd doses significantly ($P < 0.01$) increased the shoot Cd concentration and content of tobacco plants at three different temperatures of both corn cob and rice husk biochars (Table 2, 3 and 4). The Cd concentration and content at Cd0 dose of CB500 treatment were 0.48 mg $kg^{-1}$ and 3.06 g $plant^{-1}$ and both increased to 61.6 mg $kg^{-1}$ and 229.1 μg $plant^{-1}$ with the increase in Cd dose. The Cd concentration and content of tobacco shoot also significantly increased with the increase in Cd dose under the RB500 treatment (Table 2 and 3). The increase in Cd content and concentration was also observed under 400 and 600 °C treatments of corn cob and rice husk biochars. The increase in Cd concentra-

**Table 2**
Effects of corn cob biochars produced at different pyrolysis temperatures on the shoot dry matter yield, Cd concentrations and Cd content of tobacco plants under increasing Cd treatments.

| Biochar Treatment | Cd dose (mg $kg^{-1}$) | Shoot dry matter (g $plant^{-1}$) | Shoot Cd concentration (mg $kg^{-1}$) | Shoot Cd content (μg $plant^{-1}$) |
|---|---|---|---|---|
| Non-biochar | 0 | 5,02$^{a}$ | 1,07$^{c}$ | 5,39$^{c}$ |
| | 2.5 | 4,39$^{c}$ | 59,1$^{b}$ | 259,3$^{b}$ |
| | 5 | 4,64$^{b}$ | 90,5$^{a}$ | 419,7$^{a}$ |
| ***Mean*** | | ***4,68$^{B}$*** | ***50,2$^{A}$*** | ***228,1$^{A}$*** |
| Corncob CB400 | 0 | 3,77$^{ab}$ | 0,61$^{c}$ | 2,28$^{c}$ |
| | 2.5 | 3,64$^{b}$ | 53,0$^{b}$ | 192,9$^{b}$ |
| | 5 | 3,91$^{a}$ | 66,5$^{a}$ | 259,9$^{a}$ |
| ***Mean*** | | ***3,77$^{D}$*** | ***40,0$^{B}$*** | ***151,7$^{B}$*** |
| Corncob CB500 | 0 | 6,31$^{a}$ | 0,48$^{c}$ | 3,06$^{b}$ |
| | 2.5 | 4,47$^{b}$ | 46,5$^{b}$ | 207,7$^{a}$ |
| | 5 | 3,72$^{c}$ | 61,6$^{a}$ | 229,1$^{a}$ |
| ***Mean*** | | ***4,83$^{A}$*** | ***36,2$^{C}$*** | ***146,6$^{B}$*** |
| Corncob CB600 | 0 | 4,99$^{a}$ | 0,48$^{c}$ | 2,40$^{c}$ |
| | 2.5 | 4,14$^{b}$ | 42,7$^{b}$ | 176,8$^{b}$ |
| | 5 | 2,96$^{c}$ | 67,3$^{a}$ | 198,9$^{a}$ |
| ***Mean*** | | ***4,03$^{C}$*** | ***36,8$^{C}$*** | ***126,0$^{C}$*** |

The means indicated with the same capital letter in the same column are not significantly different ($p < 0.05$).
The means indicated with the same small letter in the same column are not significantly different ($p < 0.05$).

**Table 3**
Effects of rice husk biochar treatments produced at different pyrolysis temperatures on shoot matter dry matter yield, Cd concentrations and Cd content of tobacco plant under increasing Cd doses.

| Biochar Treatment | Cd Dose (mg kg$^{-1}$) | Shoot Dry matter (g plant$^{-1}$) | Shoot Cd concentration (mg kg$^{-1}$) | Shoot Cd content (μg plant$^{-1}$) |
|---|---|---|---|---|
| Non-biochar | 0 | 5,02$^{a}$ | 1,07$^{c}$ | 5,39$^{c}$ |
| | 2.5 | 4,39$^{c}$ | 59,1$^{b}$ | 259,3$^{b}$ |
| | 5 | 4,64$^{b}$ | 90,5$^{a}$ | 419,7$^{a}$ |
| ***Mean*** | | ***4,68***$^{C}$ | ***50,2***$^{A}$ | ***228,1***$^{A}$ |
| Rice husk RB400 | 0 | 6,46$^{a}$ | 0,42$^{c}$ | 2,73$^{c}$ |
| | 2.5 | 4,55$^{b}$ | 54,0$^{b}$ | 245, 8$^{b}$ |
| | 5 | 4,54$^{b}$ | 77,0$^{a}$ | 349,2$^{a}$ |
| ***Mean*** | | ***5,18***$^{A}$ | ***43,8***$^{B}$ | ***199,2***$^{B}$ |
| Rice husk RB500 | 0 | 5,21$^{a}$ | 0,55$^{c}$ | 2,85$^{c}$ |
| | 2.5 | 4,98$^{b}$ | 48,5$^{b}$ | 241,3$^{b}$ |
| | 5 | 4,70$^{c}$ | 72,3$^{a}$ | 340,1$^{a}$ |
| ***Mean*** | | ***4,97***$^{B}$ | ***40,5***$^{BC}$ | ***194,7***$^{B}$ |
| Rice husk RB600 | 0 | 5,94$^{a}$ | 0,60$^{c}$ | 3,59$^{c}$ |
| | 2.5 | 3,83$^{b}$ | 45,0$^{b}$ | 172,1$^{b}$ |
| | 5 | 3,67$^{b}$ | 70,2$^{a}$ | 257,7$^{a}$ |
| ***Mean*** | | ***4,48***$^{D}$ | ***38,6***$^{C}$ | ***144,5***$^{C}$ |

The means indicated with the same capital letter in the same column are not significantly different ($p < 0.05$).
The means indicated with the same small letter in the same column are not significantly different ($p < 0.05$).

**Table 4**
Biochar type, Cd doses, pyrolysis temperatures and interactions among the factors.

| Parameters | Dry matter | Cd concentration | Cd content | Zn concentration | Fe concentration |
|---|---|---|---|---|---|
| Biochar type (BCt) | ** | ** | ** | ns | ** |
| Pyrolysis Temperature (PT) | ** | ** | ** | ** | ** |
| Cd Dose (Cd) | ** | ** | ** | ** | * |
| BCt*PT | ** | ns | ** | ns | ** |
| BCt*Cd | ** | ** | ** | ns | ns |
| PT*Cd | ** | ** | ** | ns | * |
| BCt*PT*Cd | ** | ns | ** | ns | ns |

* Significant at $P < 0.05$ level; ** Significant at $P < 0.01$ level; ns: not significant.

tions and contents resulted in significant ($P < 0.01$) reductions in shoot Cd concentrations and contents under the treatments of all corn cob and rice husk biochars produced at different pyrolysis temperatures. The shoot Cd concentration at Cd5 dose was 90.5 mg kg$^{-1}$ under no-biochar treatment, while the same Cd dose was reduced to 66.5, 61.6 and 67.3 mg kg$^{-1}$ and 77.0, 72.3 and 70.2 mg kg$^{-1}$ with 400, 500 and 600 °C CB and RB treatments, respectively (Table 2 and 3).

Houben et al. (2013) applied 4 different biochar doses (% 0, % 1, % 5 and % 10) to a soil with Cd toxicity and grown rapeseed. Shoot Cd concentration of rapeseed plants was 3.68 mg kg$^{-1}$ in the control treatment and reduced to 3.15, 2.05 and 1.08 mg kg$^{-1}$ in other biochar doses, respectively. Namgay et al. (2010) carried out an experiment in a sandy soil growing corn and used three different biochars and Cd doses. The Cd contents of corn plants decreased with increasing biochar doses. The decrease in Cd content in plant has been connected with an increase in surface area of soil with biochar addition. The increased surface area in soil causes tight binding of Cd to the organic materials and the formation of more stable metal–organic compounds.

In parallel with the increase in the pyrolysis temperature, it was revealed that there were statistically significant ($p < 0.01$) decreases in the Cd concentration and content of the tobacco plant (Table 2, 3 and 4). While the average shoot Cd concentration under no-biochar treatment was 50.2 mg kg$^{-1}$, these average values were reduced respectively 40.0, 36.2 and 36.8 mg kg$^{-1}$ in the 400, 500 and 600 °C applications of corn cob biochar. This decrease in Cd concentration and content, depending on the pyrolysis temperature, was also observed in rice husk biochar applications. Similar to the results we obtained that biochar materials produced at high pyrolysis temperatures caused an increase in the adsorption of metals along with an increase in porosities (Chen et al., 2014). The reduction in the negative surface charges related to acidic functional groups increased the pH of biochar and, thus, higher Cd adsorption occurred on biochar surfaces. In addition, an increase in the concentration of K, Ca, Mg and P on biochar surfaces with the temperature increase may also increase ion exchange with heavy metals (Chen et al., 2014).

The physical and chemical properties of the biochars considerably vary depending on the characteristics of raw materials and the conditions of pyrolysis environment. Porosity, specific surface area, nutrient content, pH and phenolic content of biochars depend on the type of raw material and the duration and temperature of pyrolysis (Novak et al., 2009; Xu et al., 2021). The results indicated that corn cob biochar was more effective in reducing plant Cd uptake compared to rice husk biochar (Table 2 and 3). The concentration and content of Cd under Cd5 dose of CB400 were 66.5 mg kg$^{-1}$ and 259.9 μg plant$^{-1}$, while the concentration of Cd was 77.0 mg kg$^{-1}$ and the Cd content was 349.2 μg plant$^{-1}$ under RB400 and Cd5. The Cd concentration and content of shoot decreased to 61.6 mg kg$^{-1}$ and 229.1 μg plant$^{-1}$ with Cd5 dose of CB500 treatment, and to 72.3 mg kg$^{-1}$ and 340.1 μg plant$^{-1}$ with RB500 treatment. The difference in Cd uptake between two different biochar types was due to higher specific surface area of corncob biochar (Table 1). Lu et al. (2014) investigated the effects of two different doses (%1 and % 5) of bamboo straw (907.4 m$^{2}$ g$^{-1}$) and rice straw (36.7 m$^{2}$ g$^{-1}$) biochars on heavy metal uptake of *sedum plumbizincicola* plant. The treatment of bamboo straw with greater surface area was more effective in reducing heavy metal uptake to the plant. Combined effects of several processes such as ion exchange, chemisorption, complexation and surface interaction were associated to the immobilization and sorption of heavy metals on biochar surfaces (Cao et al., 2009; Ahmad et al., 2014; Lei et al., 2019). High surface area of biochars is an indication of tendency to form complexation onto biochar surfaces (Lu et al., 2012; Paz-Ferreiro et al., 2014). The physical adsorption or metal exchange between alkali and alkaline earth cations of biochars are considered the causes of the heavy metals complexation with functional groups of biochars (Lu et al., 2012; Paz-Ferreiro et al., 2014). Addition of rice straw biochar significantly decreased concentrations of Cd, Zn, and As and increased Pb concentration in shoots of wheat *(Triticum aestivum)* compared to biochars produced from rice husk and bran at 350 °C (Zheng et al., 2013).

### 3.1.1. Shoot Zn and Fe concentrations

The effects of biochar types, biochar temperatures and Cd doses on Zn and Fe concentrations of tobacco shoot was statistically significant ($P < 0.01$) (Table 4 and 5). The shoot Zn concentration of tobacco plants decreased in all temperature treatments of both corn cob and rice husk biochars under increased Cd doses (Table 5). The shoot Zn concentration under control treatment (non-biochar) at Cd0 dose was 28.6 mg kg$^{-1}$, and decreased to 27.6 and 24.6 mg kg$^{-1}$ with Cd2.5 and Cd5 doses, respectively. The shoot Zn concentration at the Cd0 dose of CB400 treatment was 25.1 mg kg$^{-1}$, while Zn concentration decreased to 23.4 at Cd2.5 and to 21.7 mg kg$^{-1}$ at Cd5 dose. The shoot Zn concentration at Cd0 dose of RB400 treatment was 25.4 and decreased to 23.5 and 21.5 mg kg$^{-1}$ at Cd2.5 and Cd5 doses, respectively. Similar trends were observed in the corn and rice husk biochars produced at 500 and 600C (Table 5). The decrease in Zn concentration with increasing Cd doses may be the result of an antagonistic relationship between Cd × Zn. Reduction of plant Zn uptake by Cd have been reported in many studies (Grant and Bailey, 1997; Grant et al., 1998; Erdem et al., 2012; Abbas et al., 2018). Higher Cd uptake in case of Zn deficiency was associated with competing of Zn and Cd which have similar chemical properties for absorption points on membranes (Grant et al., 1998; Cakmak et al., 2000) and increased membrane permeability (Cakmak and Marschner, 1988; Fu et al., 2018). The reduction in Zn concentrations was also influenced by the biochar application. The reduction of Zn uptake with biochar addition was greater in corn cob biochars compared to rice husk biochars. Mean shoot Zn concentration without biochar addition was 26.8 mg kg$^{-1}$, and reduced to mean value of 23.4 with CB400 and CB500 treatments and to 24.8 mg kg$^{-1}$ with CB600 treatment. The mean shoot Zn concentration was reduced to 23.5, 23.6 and 25.4 mg kg$^{-1}$ with RB400, RB500 and RB600 treatments, respectively (Table 5).

The increases and decreases in shoot Fe concentrations of tobacco plants were observed with increasing Cd doses of all the temperature treatments of corn cob and rice husk biochars (Table 5). There was a significant decrease in the Fe uptake of tobacco plants with increasing Cd doses of the control treatments (no biochar addition). The concentration of Fe with Cd0 dose of CB500 treatment was 126.9 mg kg$^{-1}$ and decreased to 107.5 mg kg$^{-1}$ at the Cd5 dose. Similarly, Fe concentration was 124.6 mg kg$^{-1}$ at Cd0 dose of RB500 treatment, and decreased to 104.5 mg kg$^{-1}$ at Cd5 dose (Table 5). Erdem et al. (2017) carried out a greenhouse investigating the effects of 3Cd (0, 10, and 20 mg Cd kg$^{-1}$) and 4 biochar doses (0, 1, 2 and 3) on growth and nutrient uptake of Tobacco (Xanthi/2A) plants. The researchers reported a significant decrease in the shoot Fe concentration of tobacco plants with increasing Cd doses in all biochar treatments. In contrast, biochar additions caused increases and decreases in the shoot Fe concentration of tobacco plants. The results indicated that increasing doses of Cd generally decreased the Zn and Fe concentrations of tobacco plants. The most important reason for the decrease in ion uptake of plants grown under Cd stress is related to the damage of roots and inhibition of root growth and development due to the toxicity (Salt et al., 1995). The biochar addition (including biochar type and pyrolysis temperature) usually have reported to decrease the shoot Zn and Fe concentrations of plants. This situation was associated by the improvement of physical chemical and biological properties of soils due to the addition of biochars as well as sorption of metals at a much higher level than the organic matter due to the high specific surface area, negatively charged surfaces and density of charges (Liang et al., 2006; Zhang et al., 2014).

## 4. Conclusions

The biochar type, pyrolysis temperature and Cd dose had significant ($P < 0.01$) effects on dry matter yield of tobacco plant. The increased Cd doses in the treatments of both corn and rice husk biochars produced at various temperatures caused a statistically significant reduction in the dry matter yield of tobacco plants. The effects of biochar type, temperature and Cd doses on shoot Cd concentration and content were significant at $P < 0.01$ level. The difference in Cd uptake is related to the higher specific surface area of corn cob biochar compared to rice husk biochar. The results revealed that specific surface area which has been significantly modified by the pyrolysis temperature is the most important character of biochars in the success of remediating the Cd rich soils. Biochars produced at higher pyrolysis temperatures resulted in better tobacco growth due to the immobilization of Cd ions onto biochar surfaces. However, detailed studies with various soil textures and various biochars produced by different raw materials and under different pyrolysis temperatures are needed to better understand and explain the biochar effects on plant growth under heavy metal stress.

**Table 5**

Shoot Zn and Fe concentrations (mg kg$^{-1}$) of tobacco plant under increasing Cd doses in the treatments of corn cob (CB) and rice husk (RB) biochars produced at different pyrolysis temperatures.

| Cd Dose (mg kg$^{-1}$) | Control | CB400 | CB500 | CB600 | RB400 | RB500 | RB600 |
|---|---|---|---|---|---|---|---|
| | Zn concentration (mg kg$^{-1}$) | | | | | | |
| Cd 0 | $28.6^{a}$ | 25.1 | $25.6^{a}$ | 26.8 | $25.4^{a}$ | 24.0 | $26.8^{a}$ |
| Cd 2.5 | $27.3^{ab}$ | 23.4 | $23.4^{ab}$ | 24.0 | $23.7^{a}$ | 23.6 | $25.9^{ab}$ |
| Cd 5.0 | $24.6^{b}$ | 21.7 | $21.1^{b}$ | 23.6 | $21.5^{b}$ | 23.2 | $23.4^{b}$ |
| Average | $26.8^{A}$ | $23.4^{B}$ | $23.4^{B}$ | $24.8^{B}$ | $23.5^{B}$ | $23.6^{B}$ | $25.4^{A}$ |
| **Fe concentration (mg kg$^{-1}$)** | | | | | | | |
| Cd 0 | $137.3^{a}$ | 113.4 | $126.9^{a}$ | $132.8^{ab}$ | $133.6^{a}$ | $124.6^{a}$ | 211.4 |
| Cd 2.5 | $126.2^{a}$ | 114.6 | $119.5^{ab}$ | $102.7^{b}$ | $112.9^{b}$ | $118.9^{ab}$ | 221.3 |
| Cd 5.0 | $105.9^{b}$ | 119.2 | $107.5^{b}$ | $154.3^{a}$ | $102.8^{b}$ | $104.5^{b}$ | 212.0 |
| Average | $123.1^{AB}$ | $115.7^{B}$ | $118.0^{B}$ | $129.9^{A}$ | $116.4^{B}$ | $116.0^{B}$ | $214.9^{A}$ |

The means indicated with the same capital letter in the same row are not significantly different ($p < 0.05$).
The means indicated with the same small letter in the same column are not significantly different ($p < 0.05$).

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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