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## Publisher Citation

Moon, D. H., Hwang, I., Chang, Y. Y., Koutsospyros, A., Cheong, K. H., Ji, W. H., & Park, J. H. (2017). Quality improvement of acidic soils by biochar derived from renewable materials. *Environmental Science and Pollution Research*, 24(4), 4194-4199.

## Comments

This is the authors' accepted version of the article published in *Environmental Science and Pollution Research*. The version of record can be found at <http://dx.doi.org/10.1007/s11356-016-8142-7>.

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## Quality improvement of an acidic soil by biochar

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**Abstract**

Biochar was used to improve the quality of an acidic soil. The acidic soil was treated for 1 month with both soy bean stover derived biochar and oak derived biochar in the range of 0 to 5 wt% for pH improvement and exchangeable cation enhancement. Following 1 month of treatment, the soil pH was monitored and exchangeable cations were measured. Moreover, a maize growth experiment was performed for 14 days with treated soil samples to investigate the effectiveness of the treatment. The results showed that the pH of the treated acidic soil increased by more than 2 units and the exchangeable cation values were greatly enhanced upon treatment with 5 wt% of both biochars, after 1 month of curing. Maize growth was superior in the 3 wt% biochar treated samples rather than the control sample. The presented results demonstrate the effective use of biochar derived from waste m and agricultural residues for quality improvement of acidic soils.

**Keywords** Acidic soil · Soil quality improvement · Biochar · Soil pH · Maize growth

## **Introduction**

It has been reported that poor plant growth yields are strongly associated with low soil pH because of the deficiencies and toxicities related to a number of elements (Blamey and Chapman 1982; Ok et al. 2007). Also, an acidic soil problem in the Republic of Korea has received great attention due to its adverse effects including decreased soil productivity and suboptimal plant growth. Soils in the Republic of Korea originate from acidic parent materials (mainly granite and granite gneiss) that are naturally more acidic compared to the soil generated from calcareous shale or limestone. Moreover, atmospheric deposition containing common atmospheric pollutants (i.e. SO<sub>x</sub> and NO<sub>x</sub>) of urban and/or industrial origin can intensify the acidic condition of the soil. A gradual increase in acid deposition has occurred as a result of industrialization since the late 1970s (Kim 2005). The annual mean rain pH near Seoul in the Republic of Korea ranged between 4.2 and 4.8 for the past two decades.

In order to ameliorate the acidic soil, biochar known as biomass-derived black carbon was used. Biochar is recognized as a multifunctional material that can be used in carbon sequestration, metal immobilization and soil fertilization (Awad et al. 2012; Chen et al. 2011; Uchimiya et al. 2010). Since biochar is an alkaline material and it also contains other elements, it could be expected that the soil quality of acidic soil can be improved with respect to pH and exchangeable cations. The application of biochar to acidic soil is very limited but its affordable cost makes it a very attractive option. Moreover, a maize growth experiment was conducted after the acidic soil was ameliorated with biochar. Maize is known as a very important crop for humans and animals. It has been reported that maize growth is superior in the pH ranges of 6.5 and 8 ((International Institute for Tropical Agriculture 1982). Therefore, it is expected that maize growth outside of the optimum pH ranges is adversely affected.

The objective of this study was to investigate the effectiveness of ameliorated acidic soil treated with biochar derived from soy bean stover and oak. The optimum dosage of biochar was evaluated to improve soil quality. Soil pH, exchangeable cations and maize growth were monitored and used as parameters to evaluate the quality of ameliorated acidic soil.

## **Experimental methodology**

### Acidic soil

Acidic soil was collected from a fruit garden in the Chungcheongnam do Province in the Republic of Korea at a depth of 0-30 cm below the ground surface. In order to remove large particles and provide homogeneous fractions of the soil, the acidic soil was sieved through a #10 mesh (2 mm). The soil pH of the acidic soil was measured at approximately 5.2 in accordance with the KST method (MOE 2002) at a liquid to solid ratio of 5:1. Physicochemical and mineralogical characterization data for the acidic soil is presented in Table 1. The bulk chemistry of the acidic soil determined using X-ray fluorescence (XRF) (ZSX100e, Rigaku) is presented in Table 2.

### Agents for soil quality improvement

Soybean stover and oak were used as raw feedstocks to produce biochar. Soybean stover was collected from a local agricultural field in Chungju City, Republic of Korea. Oak was obtained from Naju City, Republic of Korea. The raw feedstocks were dried in an air-forced oven at 60 °C for 3 days and ground to a size less than 1 mm. The ground soybean stover and oak were placed in a ceramic crucible with a lid and then pyrolyzed in a muffle furnace (MF 21GS, Jeio Tech, Seoul, Korea) at 7 °C min<sup>-1</sup> under limited oxygen conditions. Carbonization was performed at 700 °C and held for 3 hours followed by cooling to room temperature inside the furnace. Subsequently, the resulting biochar was stored in air-tight containers. The physicochemical properties of the biochar are listed in Table 2.

### Treatment conditions

The acidic soil was treated with both soy bean stover derived and oak derived biochars at 1wt% ~ 5wt%. All treatments were cured for 1 month. A liquid to solid ratio of 20:1 was used to ensure full hydration. The specific treatment conditions based on the percent biochar/soil ratio (dry basis) are presented in Table 3. The sample IDs are denoted as soy biochar for soy bean stover derived biochar and oak biochar for oak derived biochar.

#### Maize growth experiment

The maize growth experiment was conducted for 14 days after the acidic soil was ameliorated with biochar for 1 month. Three maize seeds (Miniheukchal, Lot no. 124201) obtained from the Jinheung Nursery Company (Republic of Korea) were sown in a small pot containing the following samples: control, 3 wt% soy bean derived biochar and 3 wt% oak derived biochar. The biochar concentration of 3 wt% was selected because the soil pH upon biochar treatment ranged in between 6.5 and 8 and the CEC values were significantly increased. The pot had three holes with diameters of about 7 mm on the bottom. A plastic screen was placed on the bottom of the pot in order to prevent soil loss. Specifically, the pot had a height of 7 cm, a top inner diameter of 5 cm and a bottom diameter of 4.8 cm.

#### Physicochemical analyses

The pH values of the acidic soil and treated soil samples were measured after curing in accordance with the Korean Standard Test (KST) method with a L/S ratio of 5:1. The exchangeable cations were determined by the KST method and the extracted solutions were analyzed by inductively coupled plasma mass spectrometry (Agilent 7500ce, USA). All sample analyses were conducted in triplicate and the averaged values were reported only if the individual measurements were within an error of 10 %. In order to monitor the accuracy and performance of the equipment, two different quality control standards and recovery spikes were used.

## Results and Discussion

### pH improvement of the acidic soil

The results of the acidic soil pH improvement using two types of biochar (soybean stover derived and oak derived) are presented in Fig. 4. The biochar treatments were beneficial in increasing soil pH. The soil pH varied in the range of approximately 5.4 - 5.8, after 7 days of curing in the control sample and increased into the pH range of 7 - 8.64 (beneficial for plant growth) upon biochar treatment at 1 - 5 wt%. Specifically for the soybean stover derived biochar treatment, the soil pH in the control sample after 7 days of curing was 5.8 and it increased to 7.42, 7.77 and 8.47 after 7 days of curing at 1, 3 and 5wt% treatments of biochar, respectively. No major changes in the soil pH were observed beyond 7 days of curing up to 28 days. This indicates that once the soil pH is improved after 7 days of curing, the soil pH can be stable for a longer period of time.

For the oak derived biochar treatment, the soil pH in the control sample was approximately 5.4 after 7 days of curing and it improved to 5.93, 6.2, 6.58, 6.97 and 7.06 after 28 days of curing upon treatments of biochar at 1, 2, 3, 4, and 5wt%, respectively. Similar to the soybean stover derived biochar treatment, no major changes in the soil pH were observed over a curing period of 28 days.

Overall, pH improvement of the acidic soil using two different types of biochar is clearly evident. The soil pH increased approximately 2.8 and 2.2 units after 28 days of curing with the addition of 5wt% soybean stover derived biochar and oak derived biochar, respectively. The soil pH increase is more pronounced with the soybean stover derived biochar than the oak derived biochar. This is mainly due to the higher content of Ca (4.63 %) in the soybean stover derived biochar as compared to the oak derived biochar. Therefore, the selection of biochar is important in improving soil pH.

### Increase in exchangeable cations upon treatment



Exchangeable cations in the control and treated samples with two types of biochar after 28 days of curing are presented in Fig. 5. The exchangeable cation values for the control samples were 1.16 cmol<sup>+</sup>/kg and 1.4 cmol<sup>+</sup>/kg, respectively for the treatments with soybean stover derived biochar and oak derived biochar, which are similar to typical values for a sandy soil. The values for exchangeable cations increased with increasing amounts of biochar. This indicated that once biochar was introduced to the acidic soil, the exchangeable cations were released into the soil and the occupied soil exchange sites (Yuan et al. 2011). The highest exchangeable cation values of 8.11 and 4.93 cmol<sup>+</sup>/kg were attained upon addition of 5 wt% soybean stover derived biochar and oak derived biochar, respectively. An exchangeable cation value of more than 5 cmol<sup>+</sup>/kg is similar to a typical value for fine sandy loams. Therefore, it can be concluded that addition of biochar enhances the ability of the treated soil with respect to the exchangeable cations. This improvement in the exchangeable cations is more pronounced upon treatment with soybean stover derived biochar rather than oak derived biochar and is attributed to the higher content of Ca, Mg, K and Na present in the soybean stover derived biochar. Therefore, the type of biochar used in remediation is important for the improvement of soil quality.

#### Maize growth experiment

Maize growth of the control and the samples treated with 3 wt% soy biochar and 3wt% oak biochar for a growth period of 14 days after seeding is presented in Table 4 and Fig. 3. The germination of the control and treated samples were 100 % and 66.7% (Table 4). The highest height of the maize plant in the control sample after 14 days of cultivation was approximately 16.9 cm. The highest maize height in both treated samples was approximately 21 cm, which was higher than the control sample (Table 4). Moreover, the plants grown in the treated soils appeared to be healthier and richer than the control sample. This indicated that the pH and CEC enhancement by biochar treatment may contribute to the growth of maize in ameliorated acidic soil. It has been reported that when optimum conditions for pH and CEC are developed in the acidic soil, maize growth was superior (Onwuka et al. 2009; Moon et al. 2014a; Moon et al. 2014b). Therefore, the optimum use of biochar in

acidic soil could be beneficial to plant growth since the quality of acidic soil was improved.

## **Conclusions**

This study explores sustainable uses of biochar derived from waste plant and agricultural residues as renewable resources in environmental applications. Biochar derived from soybean stover and oak were used for acidic soil quality improvements. Soil quality was evaluated based on pH and CEC improvement. Following the quality improvement of the acidic soil, the maize growth experiment was performed to evaluate the effectiveness of the treatment. The treatment results showed that the soil pH was increased by 2.8 and 2.2 units after 28 days of curing, upon treatment with 5wt% soy bean stover biochar and oak derived biochar, respectively. The soy bean stover biochar outperformed the oak derived biochar due to high Ca content. The exchangeable cation values increased from 1.16 to 8.11  $\text{cmol}^+/\text{kg}$  and 1.4 to 4.93  $\text{cmol}^+/\text{kg}$  upon soy bean stover biochar and oak derived biochar, respectively, indicating that the soil quality was improved. Moreover, maize growth was superior in both biochar treated samples and plant grown appeared to be healthier and richer as compared to the control sample. Overall, considering the pH, exchangeable cations and maize growth results, it could be concluded that the 3wt% biochar treatment to the acidic soil was the most effective treatment investigated.

## **Acknowledgement**

This study was supported by the Korea Ministry of Environment as The GAIA (Geo-Advanced Innovative Action) Project (No. 173-111-040).

## **References**

Ahmad M, Hashimoto Y, Moon DH, Lee SS, Ok YS (2012) Immobilization of lead in a Korean military shooting

- range soil using eggshell waste: an integrated mechanistic approach. *J Hazard Mater* 209-210:392-401
- Awad YM, Blagodatskaya E, Ok YS, Kuzyakov Y (2012) Effects of polyacrylamide, biopolymer and biochar on decomposition of soil organic matter and plants residues as determined by <sup>14</sup>C and enzyme activities. *Eur J Soil Biol* 48:1-10
- Cao X, Ma LQ, Chen M, Hardison DW, Harris WG (2003) Weathering of lead bullets and their environmental effects at outdoor shooting ranges. *J Environ Qual* 32:526-534
- Cao X, Ma LQ, Chen M, Hardison DW, Harris WG (2003a) Lead transformation and distribution in the soils of shooting ranges in Florida, USA. *Sci Total Environ* 307:179-189
- Cao X, Ma LQ, Chen M, Hardison DW, Harris WG (2003b) Weathering of lead bullets and their environmental effects at outdoor shooting ranges. *J Environ Qual* 32:526-534
- Cao X, Ma LQ, Chen M, Singh SP, Harris WG (2002) Impacts of phosphate amendments on lead biogeochemistry at a contaminated site. *Environ Sci Technol* 36:5296-5304
- Cao X, Ma LQ, Chen M, Singh SP, Harris WG (2002) Impacts of phosphate amendments on lead biogeochemistry at a contaminated site. *Environ Sci Technol* 36:5296-5304
- Chen B, Chen Z, Lv S (2011) A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. *Bioresour Technol* 102:716-723
- Chrastný V, Komárek M, Hájek T (2010) Lead contamination of an agricultural soil in the vicinity of a shooting range. *Environ Monit Assess* 162:37-46
- Craig JR, Rimstidt JD, Bonnaffon CA, Collins TK, Scanlon PF (1999) Surface water transport of lead at a shooting range. *B Environ Contam Tox* 63:312-319
- Dermatas D, Cao X, Tsaneva V, Shen G, Grubb DG (2006) Fate and behavior of metal(loid) contaminants in an organic matter-rich shooting range soil: Implications for remediation. *Water Air Soil Poll* 6:143-155
- Dermatas D, Menouno N, Dutko P, Dadachov M, Arienti P, Tsaneva V (2004) Lead and copper contamination in small arms firing ranges. *Global Nest J* 6:141-148
- Gougar MLD, Scheetz BE, Roy DM (1996) Ettringite and C-S-H Portland cement phases for waste ion

- immobilization: A review. *Waste Manage* 4:295-303
- Gräfe M, Singh B, Balasubramanian M (2007) Surface speciation of Cd(II) and Pb(II) on kaolinite by XAFS spectroscopy. *J Colloid Interf Sci* 315:21-32
- Hashimoto Y, Matsufuru H, Takaoka M, Tanida H, Sato T (2009) Impacts of chemical amendments and plant growth on lead speciation and enzyme activities in a shooting range soil: an X-ray absorption fine structure investigation. *J Environ Qual* 38:1420-1428.
- Keller WD (1964) Processes of origin and alteration of clay minerals. In C. I. Rich & G. W. Kunze (Eds.), *Soil clay mineralogy* (pp. 3-76). Chappel Hill: University of North Carolina
- Knechtenhofer LA, Xifra IO, Scheinost AC, Flührer H, Kretzschmar R (2003) Fate of heavy metals in a strongly acidic shooting range soil: Smallscale metal distribution and its relation to preferential water flow. *J Plant Nutr Soil Sc* 166:84-92
- Lin SL, Cross WH, Chian ESK, Lai JS, Giabbai M, Hung CH (1996) Stabilization and solidification of lead in contaminated soils. *J Hazard Mater* 48:95-110
- Lin Z (1996) Secondary mineral phases of metallic lead in soils of shooting ranges from Orebro County, Sweden. *Environ Geol* 27:370-375
- Lin Z, Comet B, Qvarfort U, Herbert R (1995) The chemical and mineralogical behaviour of Pb in shooting range soils from central Sweden. *Environ Pollut* 89:303-309
- Long RP, Zhang X (1998) Treating lead-contaminated soil by stabilization and solidification. *Transp Res Rec* 1615:72-78
- MOE (2002) *The Korean Standard Leaching Test (KSLT) Methods for soils* (p. 225). Gwachun, Kyunggi: Korean Ministry of Environment (in Korean)
- MOE (2005) *The development of hybrid electrokinetic remediation technique using solar energy on shooting range soils contaminated by heavy metals*, pp 40-63.
- Moulin I, Stone WE, Sanz J, Bottero JY, Mosnier F, Haehnel C (1999) Lead and zinc retention during hydration of tri-calcium silicate: a study by sorption isotherms and <sup>29</sup>Si nuclear magnetic resonance spectroscopy.

- Langmuir 15:2829-2835
- Ok YS, Lim JE, Moon DH (2011) Stabilization of Pb and Cd contaminated soils and soil quality improvements using waste oyster shells. *Environ Geochem Hlth* 33:83-91
- Puls RW, Powell RM, Clark D, Eldred CJ (1991) Effects of pH, solid/solution ratio, ionic strength, and organic acids on Pb and Cd sorption on kaolinite. *Water Air Soil Poll* 57-58:423-430
- Ravel B, Newville M (2005) Athena, artemis, hephaestus: data analysis for X-ray absorption spectroscopy using IFEFFIT, *Journal of Synchrotron Radiation* 12:537-541
- Robinson BH, Bischofberger S, Stoll A, Schroer D, Furrer G, Roulier S, et al. (2008). Plant uptake of trace elements on a Swiss military shooting range: Uptake pathways and land management implications. *Environ Pollut* 153:668-676
- Rose J, Moulin I, Hazemann J-L, Masion A, Bertsch PM, Bottero J-Y, Mosnier F, Haehnel C (2000) X-ray absorption spectroscopy study of immobilization processes for heavy metals in calcium silicate hydrates: 1. case of lead. *Langmuir* 16:9900~9906
- Scheckel KG, Ryan JA (2002) Effects of aging and pH on dissolution kinetics and stability of chloropyromorphite. *Environ Sci Technol* 36:2198-2204
- Sorvari J, Antikainen R, Pyy O (2006) Environmental contamination at Finnish shooting ranges-the scope of the problem and management options. *Sci Total Environ* 366:21-31
- Stansley W, Roscoe DE (1996) The uptake and effects of lead in small mammals and frogs at a trap and skeet range. *Arch Environ Con Tox* 30:220-226
- Uchimiya M, Wartelle LH, Lima IM, Klasson KT (2010) Sorption of deisopropylatrazine on broiler litter biochars. *J Agric Food Chem* 58:12350-12356
- Ure AM (1995) In: Alloway BJ (ed) *Heavy metals in Soils*, Glasgow. Chapman & Hall, Boca Raton
- USEPA (2005) Best management practices for lead at outdoor shooting ranges, EPA-902-B-01-001.
- USEPA (1992) *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846*, third ed., Method 1311, U.S. EPA, Washington DC

USGS (2007) Lead in April 2007. Mineral industry surveys. US Geological Survey

Yuan J-H, Xu R-K, Wang N, Li J-Y (2011) Amendment of acid soils with crop residues and biochars. *Pedosphere* 21:302-308

Zhang P, Ryan JA (1999) Transformation of Pb(II) from cerrusite to chloropyromophite in the presence of hydroxyapatite under varying conditions of pH. *Environ Sci Technol* 33:625-630

**Table 1** Physicochemical properties of the acidic soil

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Soil properties	Acidic soil
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Soil pH	5.02±0.21
Organic matter content (%) <sup>a</sup>	7.6
Cation exchange capacity (meq/100mg) <sup>b</sup>	1.16
Composition (%) <sup>c</sup>	
Sand	97.5
Silt	1.6
Clay	0.9
Texture <sup>d</sup>	Sand

<sup>a</sup>Organic matter content (%) was calculated from measured loss-on-ignition (LOI) (Ball 1964, FitzPatrick 1983)

<sup>b</sup>Cation exchange capacity (CEC) measured by USEPA method 9081

<sup>c</sup>Sand, 50-2,000 µm; silt, 2-50 µm; clay, < 2 µm

<sup>d</sup>Soil texture suggested by the United States Department of Agriculture (USDA)

**Table 2** Physicochemical properties of acidic soil, soybean stover derived biochar and oak derived biochar

	Acidic soil		Soybean stover derived biochar	Oak derived biochar
Major chemical properties		Major chemical properties		
SiO <sub>2</sub>	61	C	85.3	99
Al <sub>2</sub> O <sub>3</sub>	19.80	Na	0.0314	0.0129
TiO <sub>2</sub>	0.72	Mg	0.9	0.0461
Fe <sub>2</sub> O <sub>3</sub>	4.56	Al	0.149	0.0057
MnO	0.07	Si	0.436	0.0147
MgO	0.70	P	0.914	0.0181
CaO	0.2	S	0.244	0.0075
Na <sub>2</sub> O	0.22	Cl	0.075	0.0013
K <sub>2</sub> O	4.67	K	6.63	0.357
P <sub>2</sub> O <sub>5</sub>	0.24	Ca	4.63	0.533
SO <sub>3</sub>	0.04	Fe	0.199	0.0033
pH (1:5)	5.02	pH (1:5)	10.5	10.25

**Table 3** Test matrix for untreated and treated samples



Sample ID	Acidic soil	Soybean derived biochar (wt%)	Oak derived biochar (wt%)	L:S ratio
Control	√	0	0	20:1
Soy biochar1	√	1	-	20:1
Soy biochar2	-	-	-	20:1
Soy biochar3	√	3	-	20:1
Soy biochar4	-	-	-	20:1
Soy biochar5	√	5	-	20:1
Oak biochar1	√	-	1	20:1
Oak biochar2	√	-	2	20:1
Oak biochar3	√	-	3	20:1
Oak biochar4	√	-	4	20:1
Oak biochar5	√	-	5	20:1

**Table 4** Maize plant growth results

Sample ID	Germination rate (%)	Height (cm)
Control	100	16.9
Soy biochar3	66.7	20.5
Oak biochar3	66.7	21

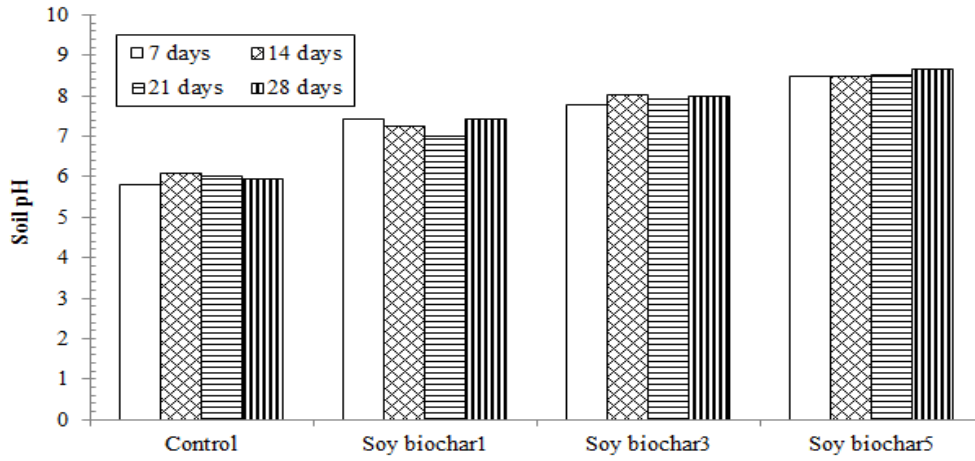
**Fig. 1.** Soil pH values for samples treated with soy bean stover derived biochar at 1wt%, 3wt% and 5wt% after 28 days of curing (a) and soil pH values for samples treated with derived biochar at 1wt%, 2wt%, 3wt%, 4wt% and 5wt% oak after 28 days of curing (b)

**Fig. 2.** Changes in exchangeable cations upon the soy bean stover derived biochar treatment (a) and oak derived biochar treatment (b)

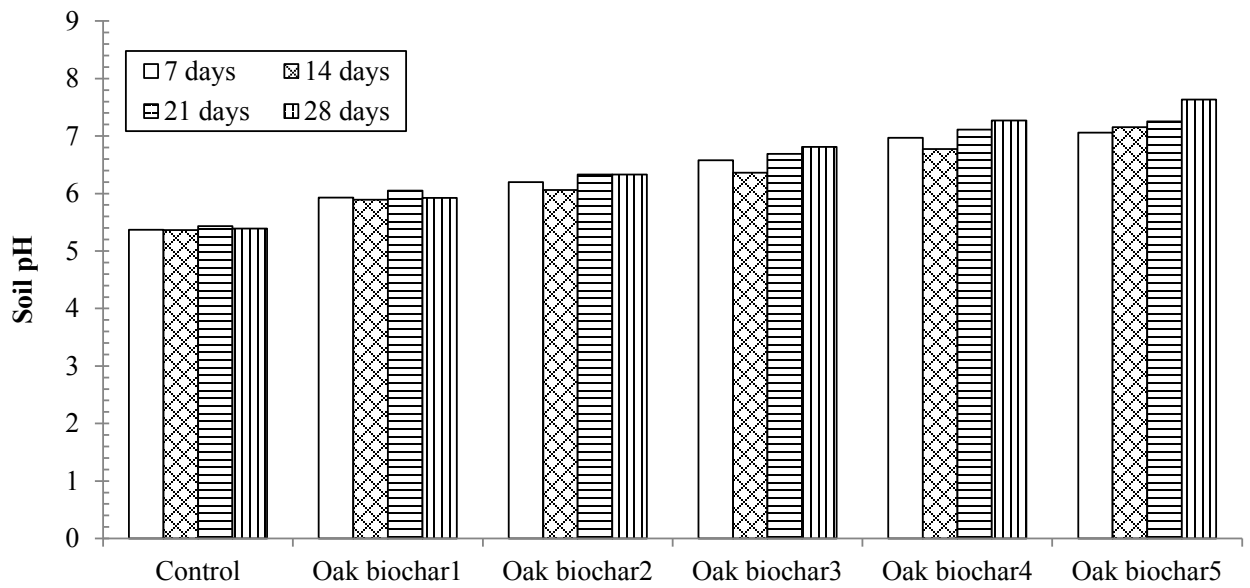
**Fig. 3.** Maize growth after 14 days of seeding in the following samples: control (a), 3 wt% soy biochar (b), 3 wt% oak biochar (c)

Fig. 1

(a)

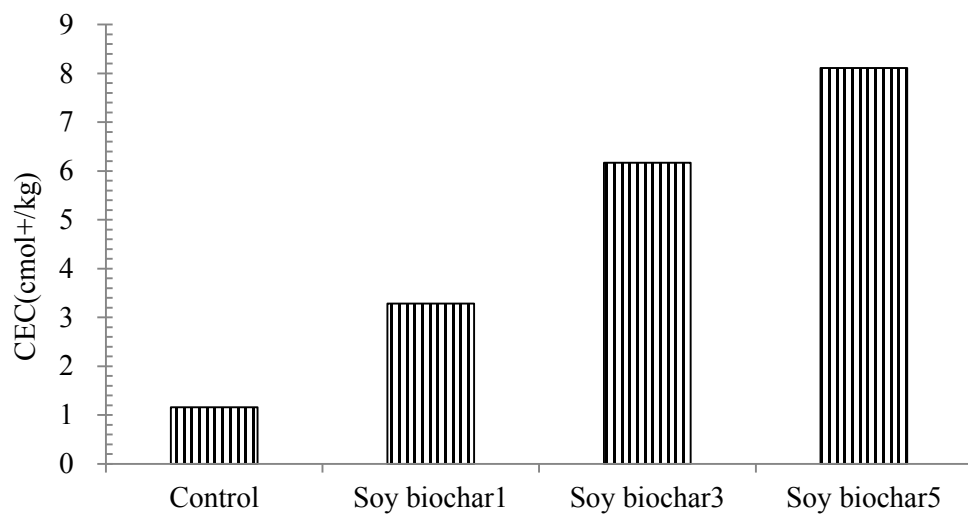


(b)

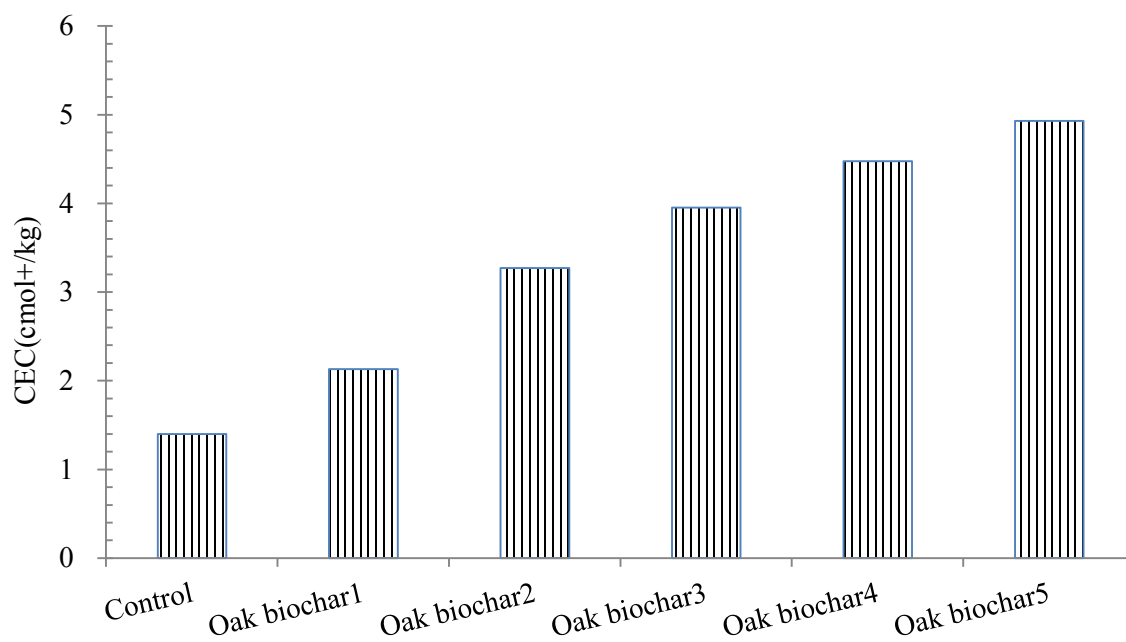


**Fig. 2**

(a)

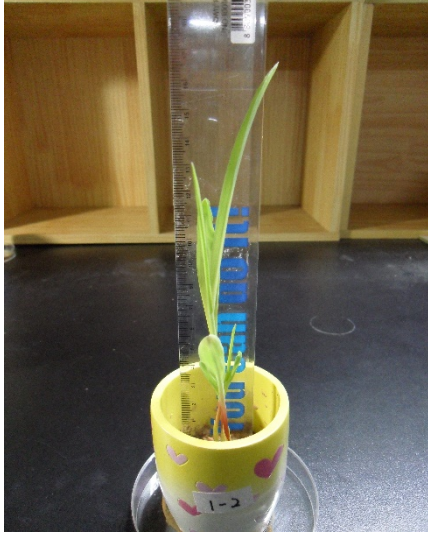


(b)



**Fig. 3.**

(a)



(b)



(c)

