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Slow pyrolyzed biochars from crop residues for soil metal(loid) immobilization and microbial community abundance in contaminated agricultural soils

Avanthi Deshani Igalavithana [a], Jinje Park [b], Changkook Ryu [b], Young Han Lee [c], Yohey Hashimoto [d], Longbin Huang [e], Eilhann E. Kwon [f], Yong Sik Ok [a, *], Sang Soo Lee [a, **]

[a] Korea Biochar Research Center & School of Natural Resources and Environmental Science, Kangwon National University, Chuncheon 24341, Republic of Korea
[b] School of Mechanical Engineering, Sungkyunkwan University, Suwon 16419, Republic of Korea
[c] Division of Plant Environmental Research, Gyeongsangnam-do Agricultural Research & Extension Services, Jinju 52773, Republic of Korea
[d] Department of Bioapplication and Systems Engineering, Tokyo University of Agriculture and Technology, Tokyo 184-8588, Japan
[e] Centre for Mined Land Rehabilitation, Sustainable Minerals Institute, The University of Queensland, Brisbane, Queensland 4072, Australia
[f] Department of Environment and Energy, Sejong University, Seoul 05006, Republic of Korea

HIGHLIGHTS

- Slow pyrolyzed biochars from three crop residues immobilized Pb in soils.
- Biochars were efficient in improving soil chemical properties.
- Biochars did not enhance As immobilization in soils.
- Biochars were not beneficial for soil microbial community abundance.
- Biochars were not beneficial for increase in soil dehydrogenase activity.

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ABSTRACT

This study evaluated the feasibility of using biochars produced from three types of crop residues for immobilizing Pb and As and their effects on the abundance of microbial community in contaminated lowland paddy (P-soil) and upland (U-soil) agricultural soils. Biochars were produced from umbrella tree [*Maesopsis eminii*] wood bark [WB], cocopeat [CP], and palm kernel shell [PKS] at 500 °C by slow pyrolysis at a heating rate of 10 °C min^{-1}. Soils were incubated with 5% (w w^{-1}) biochars at 25 °C and 70% water holding capacity for 45 d. The biochar effects on metal immobilization were evaluated by sequential extraction of the treated soil, and the microbial community was determined by microbial fatty acid profiles and dehydrogenase activity. The addition of WB caused the largest decrease in Pb in the exchangeable fraction (P-soil: 77.7%, U-soil: 91.5%), followed by CP (P-soil: 67.1%, U-soil: 81.1%) and PKS (P-soil: 9.1%, U-soil: 20.0%) compared to that by the control. In contrast, the additions of WB and CP increased the exchangeable As in U-soil by 84.6% and 14.8%, respectively. Alkalinity and high phosphorous content of biochars might be attributed to the Pb immobilization and As mobilization, respectively. The silicon content in biochars is also an influencing factor in increasing the As mobility. However, no considerable effects of biochars on the microbial community abundance and dehydrogenase activity were found in both soils.

1. Introduction

A large amount of crop residues is generated worldwide, and their proper use as an initial feedstock for many applications is very desirable because of the carbon-rich composition and renewability

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* Corresponding author.
** Corresponding author.
E-mail addresses: soilok@kangwon.ac.kr (Y.S. Ok), sslee97@kangwon.ac.kr (S.S. Lee).

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of the crop residues (Colantoni et al., 2016). The production of global crop residues has reached >3.7 Pg y^{-1}, and its potential increase can be >1.3 Pg y^{-1}. The environmentally benign practices of crop residues in the form of biochars are widely considered for soil carbon sequestration or soil quality improvement (Ahmad et al., 2014b; Kim et al., 2015; Rajapaksha et al., 2015).

Biochars, a carbon-rich mixture of in/organic compounds, are generated as a byproduct in pyrolysis of feedstocks at limited oxygen conditions (Lehmann and Joseph, 2009). The feedstock properties such as density, particle size, particle shape, thermal conductivity, and permeability, and the intrinsic properties (*i.e.*, lignin, cellulose, and hemicelluloses contents, composition of inorganic compounds, moisture content, etc.) are the important factors for determining the properties of biochars (Joseph et al., 2009). In addition to the feedstock properties, the pyrolytic conditions also determine the physicochemical properties of biochars (Ahmad et al., 2014b). On the basis of these results, research studies were conducted with various pyrolytic conditions (*i.e.*, slow/fast pyrolysis, gasification, etc.) to generate biochars (Manyà, 2012; Poucke et al., 2016). The chemical performance of biochars is dependent on its physiochemical properties, including surface area, porous structure, surface functional groups, ash content, crystalline and amorphous carbon structures, and elemental composition (Ahmad et al., 2013; Inyang et al., 2016; Qian et al., 2015; Rajapaksha et al., 2014). An increase in biochar surface area mainly results from the liberation of volatile matter from the pore spaces with increasing pyrolysis temperature (Ahmad et al., 2014a). The reported biochar surface area ranged from 0.1 to >900 m^2 g^{-1} (UC Davis Biochar database, 2015). Generally, slow pyrolyzed biochars have a large surface area and high carbonization degree because low heating rates and long holding times facilitate the removal of volatile matter and the systematic arrangement (*i.e.*, grapheme-like structures) of organic carbon structures (Manyà, 2012). Therefore, the slow pyrolyzed biochars have properties favorable for soil amendment, soil fertility improvement, and contaminant immobilization, in addition to its benefits in soil carbon sequestration (Gómez et al., 2016; Pandey et al., 2016).

Although biochars have been known as soil amendments to effectively immobilize soil heavy metals, the efficacy of slow pyrolyzed biochars on soil microorganisms has not been well investigated yet (Ahmad et al., 2014a, 2016a,b; Anderson et al., 2011; Lehmann et al., 2011; Luo et al., 2013; Oleszczuk et al., 2014). Scientists have reported contrasting observations in microbial communities following biochar application to soils mainly because of the differences in biochar and soil properties and biochar application rates (Luo et al., 2013). The readily available carbon and nutrients, large surface area, and porous structures of the biochars are considered as the favorable factors for soil microbial growth (Lehmann et al., 2011). Among these factors, the readily available carbon and nutrients are reported as the most important factor for improving the microbial community abundance within a short term (Kolb et al., 2009). Biochars produced at a low temperature contain a high amount of carbon, which is readily available (Ahmad et al., 2014b). However, the experimental evidence associated with soil microbial community abundance and mass transportation (*i.e.*, carbon and nutrient) from biochars to microorganisms is not fully established (Lehmann et al., 2011). In addition, the role of biochars in microbial abundance in metal-contaminated soils remains largely unknown. The present study hypothesizes that the high metal adsorption capacity of biochars because of their large surface area and high aromaticity could lower the biotoxicity of metals in contaminated soils, thereby improving the soil microbial community abundance in soil within a short term. Reduced biotoxicity of metals also helps in *in-situ* biogeochemical processes for organic matter decomposition and nutrient cycling in the soil. To evaluate our hypothesis, we produced biochars at 500 °C by slow pyrolysis to increase the surface area and aromaticity and tested their effectiveness in Pb and As immobilizations and microbial community abundance in contaminated agricultural soils. Three types of crop residues containing large amounts of lignin were used as the biomass for producing slow pyrolized biochars to obtain high aromaticity.

The objectives of this study are to evaluate (1) the efficacy of immobilization of heavy metals in contaminated agricultural soils by using biochars produced from umbrella tree (*Maesopsis eminii*) wood bark (WB), cocopeat (CP), and palm kernel shell (PKS), (2) the changes in chemical properties of heavy metal-contaminated agricultural soils with the incorporation of three biochars, and (3) the microbial community abundance and activity in heavy metal-contaminated agricultural soils with the incorporation of three biochars, using laboratory incubation. Sequential extraction of metals was used to analyze the metal immobilization by biochars. The fatty acid methyl ester (FAME) analysis and the dehydrogenase activity were used to evaluate the microbial community and the activity in heavy metal-contaminated soils treated with biochars, respectively.

2. Materials and methods

2.1. Biochars

Biochars were produced from three crop residues collected from Indonesia: umbrella tree (*M. eminii*) WB, CP, and PKS, as reported in a previous study by Lee et al. (2013a, b). Slow pyrolysis was performed at a heating rate of 10 °C min^{-1} from ambient temperature to 500 °C and holding it at 500 °C for 1 h to produce biochars. A complete anaerobic condition was maintained inside the furnace by N_2 gas at a purging rate of 1.5 L min^{-1}. The biochar properties are listed in Table 1 (Lee et al., 2013a, b). The graphitized carbon structures and the surface functional groups of biochars were characterized by Raman spectrophotometry (ARAMIS, Horiba, Japan) and Fourier transform infrared spectroscopy (FT-IR; Frontier, PerkinElmer, UK), respectively.

2.2. Soil collection and characterization

Contaminated agricultural soils were collected from a lowland paddy field (P-soil), which is located near the closed Seoseong mine at Seosan-si (36.78° N, 126.45° E) in Chungnam-do, Korea, and from an upland fallowed agricultural field (U-soil), which is located near the Tancheon mine at Gongju-si (36.44° N, 127.12° E) in Chungnam-do, Korea.

Soils were air dried and screened using a 2-mm sieve. Soil texture (by the pipette method), pH and electrical conductivity (1:5 soil to deionized water), exchangeable cations (Ca^{2+}, K^{+}, Mg^{2+}, and Na^{+}), exchangeable Pb (ammonium acetate at pH 7; ICP-OES, Optima 7300 DV, Perkin-Elmer, USA), and total As and Pb (MARS, HP-500 plus, CEM Corp., NC, USA) were determined (Ahmad et al., 2016a; Smith and Mullins, 1991; USEPA, 2007).

2.3. Soil incubation experiment

A short-term laboratory incubation study was conducted to evaluate the biochar effects on As and Pb immobilizations and soil microbial community abundance. Biochar incorporation could increase the soil microbial community abundance in short term because of its volatile matter supplement (Lehmann et al., 2011). A mixture of 100 g soil and 5% (w w^{-1}) biochar was placed in a 600-mL high-density polyethylene bottle. The water content in the bottle was adjusted to 70% water holding capacity and incubated at