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# Biochar-induced Metals Immobilization in the Soil as Affected by Citric Acid

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**Abstract :** Reducing trace elements' mobility and bioavailability through amendment addition, especially biochar (BC), is a cost-effective and efficient method to address their toxicity in the soil environment. However, the low molecular weight organic acids (LMWOAs) in the rhizosphere could affect BC's efficiency to stabilize trace metals as the LMWOAs could either mobilize or fix metals in the soils. Therefore, understanding the BC's and LMWOAs' interaction mechanisms on metals stabilization in the rhizosphere is crucial. The present study explored the impact of BC derived from rice husk and citric acid (CA) and the combination of BC and CA on the redistribution of cadmium (Cd), lead (Pb), and zinc (Zn) among their geochemical forms through incubation experiment. The changes of zeta potential and X-ray diffraction (XRD) pattern of BC and BC-amended soils to investigate the probable mechanisms of trace elements' immobilization by BC under the CA attack were also examined. The rice husk BC at 5% (w/w) was mixed with the air-dry soil (an Anthrosols) contaminated with Cd, Pb, and Zn in the plastic pot. The 2, 5, 10, and 20 mM kg-1 (w/v) of CA were added separately into the pot. All the ingredients were mixed thoroughly with the soil. A control (CK) treatment was also prepared without BC and CA addition. After 7, 15, and 60 days of incubation with 60% (w/v) moisture level at 25 °C, the incubated soils were determined for pH and EC and were sequentially extracted to assess the metals' transformation in soil. The electronegative charges and XRD peaks of BC and BC-amended soils were also measured. Compared to CK, the application of BC, low level of CA (2 mM kg-1 soil) (CA2), and BC plus the low concentration of CA (BC-CA2) considerably declined the acid-soluble Cd, Pb, and Zn in which BC-CA2 was found to be the most effective treatment. The reversed trends were observed concerning the high levels of CA (>5-20 mM kg-1 soil) and the BC plus high concentrations of CA treatments. BC-CA2 changed the highest amounts of acid-soluble and reducible metals to the oxidizable and residual forms with time. The most increased electronegative charges of BC-CA2 indicate its (BC-CA2) highest Cd, Pb, and Zn immobilizing efficiency, probably through metals adsorption and fixation with the negative charge sites. The XRD study revealed the presence of P, O, CO32-, and Cl1- in BC, which might be responsible for the precipitation of CdCO3, pyromorphite, and hopeite in the case of Cd, Pb, and Zn immobilization, respectively. The findings depicted that the low concentration of CA increased metals' stabilization, whereas the high levels of CA enhanced their mobilization. The BC-CA2 emerged as the best amendment among treatments for metals stabilization in contaminated soils.

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