Agronomic waste-derived biochar for concurrent stabilization of multiple heavy metals in agricultural soil: Effect of feedstock variety and pyrolysis temperature

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Biochar (BC) has been advocated as a low-cost, low-impact, and eco-friendly soil amendment material alternative to activated carbon for heavy metal immobilization in contaminated soils. Yet, the effects of feedstock variety and pyrolysis temperature on the synthetic BC used to remediate arable soils contaminated with multiple heavy metals have been relatively understudied. Here, we examined BC samples prepared by pyrolyzing rice husk and camphor tree leaves at 300 and 600 °C (designated as RB300, RB600, LB300 and LB600, respectively) for their capacity of metal-adsorption in aqueous solution, as well as metal-immobilization in the paddy soil contaminated with Cd, Cu, and Zn. A decrease in porewater concentrations of these metals is used as a proxy for the efficient mitigation of *in situ* metal bioavailability. Characterization of the synthetic BCs showed that elevated pyrolysis temperature resulted in BCs with higher pH, surface area, and carbon content, but lower oxygen content and functional group abundance (Table 1). Batch adsorption experiments conducted in DI water with the mono-, duo- and tri-metal species at environmentally relevant concentrations (i.e., ppb levels) revealed that BCs synthesized at lower pyrolysis temperature exhibited higher metal adsorption capacity (Fig. 1). Of the three metals, the adsorption followed the order of Cu(II) > Cd(II) > Zn(II) to all BC samples but LB30, on which Cd(II) outcompete Cu(II). However, soil incubation experiments showed that while 5% BCs amendment indeed led to significant porewater metal reductions, BCs prepared at higher pyrolysis temperature surprisingly showed more effectiveness of metal stabilization (Fig. 1 & 2a). This discrepancy might come from organic matter released from or associated with the soil that interfered in the metal speciation. Nonetheless, compared to rice husk, BCs made from camphor tree leaves showed better efficacy of metal sequestration in both matrices (i.e., the aqueous solution and soil phase). When results of the sorption isotherms were fitted with a linear model and used to predict porewater reductions for the metals in flooded soils, the model only provided good fits for RB300- and LB300-treated soil samples (Fig. 2b-d), suggesting that the role of soil organic matter demands further investigations. Taken together, this study demonstrates that BCs synthesized using agronomic solid wastes have the potential for use in *in situ* treatment of farmland soils polluted by multiple heavy metals, and also provides a basis for selecting carbonaceous precursors.

Table 1. Selected physical and chemical properties of feedstock materials and synthetic biochar samples

Properties	Rice husk	RB300	RB600	Leaf	LB300	LB600
Moisture (%)	4.22 ± 0.08	2.32 ± 0.08	1.81 ± 0.08	7.74 ± 0.16	3.13 ± 0.10	2.50 ± 0.33
Ash content (%)	15.34 ± 0.05	22.89 ± 0.01	35.21 ± 0.04	7.64 ± 0.02	8.01 ± 0.50	19.03 ± 0.11
C %	42.32 ± 0.01	50.23 ± 0.01	56.07 ± 0.17	48.41 ± 0.12	55.19 ± 0.04	63.91 ± 0.01
H %	6.30 ± 0.18	4.26 ± 0.20	2.50 ± 0.13	6.70 ± 0.02	5.59 ± 0.29	2.93 ± 0.20
N %	0.88 ± 0.02	1.08 ± 0.03	0.94 ± 0.04	1.25 ± 0.01	1.48 ± 0.08	1.47 ± 0.06
O %	41.80 ± 0.04	23.54 ± 0.02	7.01 ± 0.09	39.59 ± 0.24	32.19 ± 0.14	16.64 ± 0.28
S %	0.07 ± 0.03	-	-	0.09 ± 0.01	0.02 ± 0.00	0.03 ± 0.00
O/C	0.99 ± 0.00	0.47 ± 0.00	0.13 ± 0.00	0.82 ± 0.00	0.58 ± 0.00	0.260± 0.00
H/C	0.14 ± 0.00	0.09 ± 0.00	0.05 ± 0.00	0.14 ± 0.00	0.10 ± 0.01	0.05 ± 0.00
(O+N)/C	1.01 ± 0.00	0.49 ± 0.00	0.14 ± 0.00	0.84 ± 0.01	0.61 ± 0.01	0.28 ± 0.00
SA (m^2/g)		1.05	224.91		1.17	205.10
Total PV (cm^3/g)		0.005	0.142		0.004	0.146
Pore size (nm)		19.59	3.68		19.30	5.74
pH		6.48 ± 0.01	8.20 ± 0.14		6.03 ± 0.03	7.90 ± 0.13

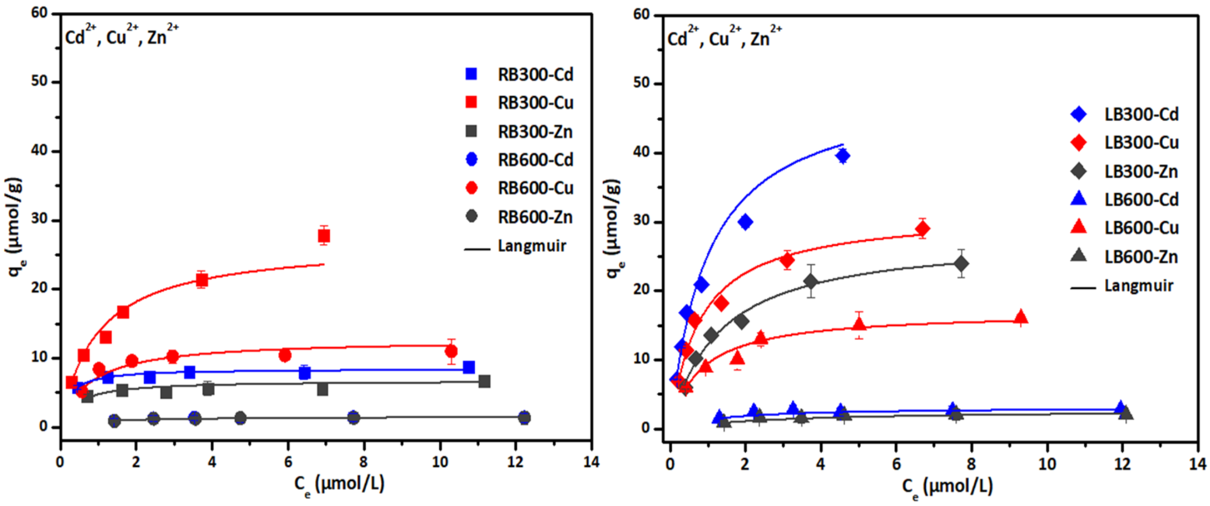

Figure 1. Adsorption isotherms of a ternary system of Cd(II), Cu(II) and Zn(II) onto rice husk (left)- and camphor tree leaf (right)-derived biochars prepared under 300 or 600 °C pyrolysis conditions, namely RB300, RB600, LB300, and LB600.

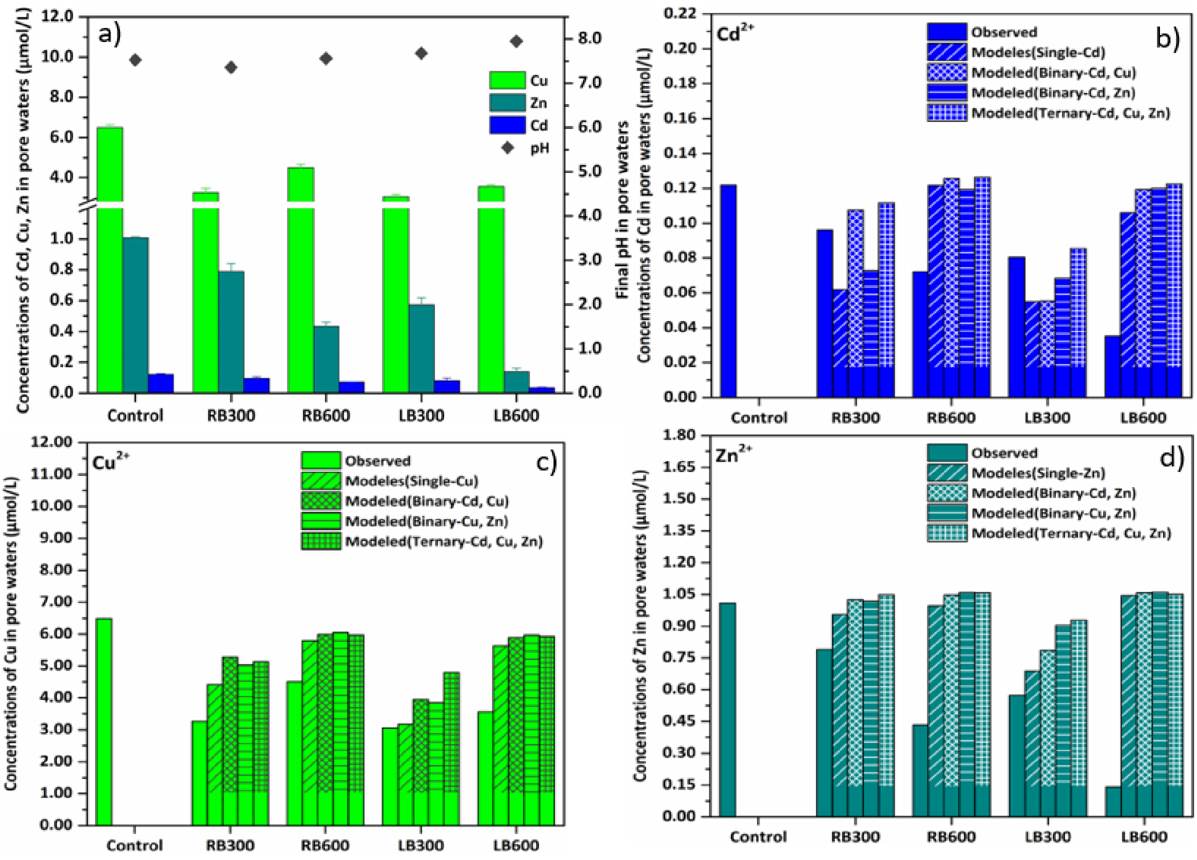

Figure 2. Measured (a) and modeled (b-d) porewater Cd(II), Cu(II), and Zn(II) concentrations in contaminated paddy soils amended with and without (i.e., control) 5% biochar. Both treated and untreated soils were incubated with DI water for two weeks before analysis of metals in porewater.