Original Research Article

Agro waste biochar to reduce the leaching of heavy metals from Ultisol soil amended with coal fly ash

Abstract

This study tested the hypothesis that co-application of biochar organic soil amendment together with coal fly ash could positively change the bioavailability and leaching characteristics of heavy metals in sandy soils by various fixing mechanisms. We tested the effect of biochar produced from avocado branch cut biomass on the leaching of heavy metals from sandy Ultisol added with coal fly ash. Column leaching tests were conducted with Ultisol soils amended with biochar and coal fly ash at 5 tons/ha rate. The results showed the presence of heavy metal in the leachate of fly ash added soil. Application of biochar significantly reduced the leachability of all the detected heavy metals in the study. The reduction rates were up to 55%. Therefore, biochar is highly effective in stabilizing the heavy metals added from coal fly ash to minimize the risk of environmental contamination.

Key words- Soil amendment, Ultisol, Coal fly ash, Biochar, Heavy metals

Highlights

1. Heavy metal contamination is a major constraint of using coal fly ash as a soil amendment.
2. Co-application of agro waste biochar with coal fly ash was tested using column leaching experiments.
3. The leachate concentration of Zn, Pb, As, Cd, Ni, Cr, Se and Mo were measured under simulated rainfall conditions.
4. The concentration of above elements in the leachates of fly ash added soils were notable.
5. Biochar significantly reduced the leaching trend of heavy metals from coal fly ash amended soil.

1. INTRODUCTION

Soil amendment capacity of coal combustion fly ash has been extensively researched over the past three decades across a wide range of soil types. Accordingly, coal fly ash has been found to help in improving the physico-chemical properties of loose structured sandy Ultisols occur in southeastern agricultural regions of USA, by various mechanisms. Yet, as the research literature states coal fly ash contains some biologically toxic elements in concentrations that greatly exceed their concentrations in soil [1, 2]. Hence continuous loading of soils with fly ash has a tendency to accumulate these elements in the soils and end up in food chains and ground water to cause serious animal and human health risks [1]. Especially, the soils being sandy and loose structured plus high rainfall of the region aggravate the situation to account for a large leaching losses of toxic elements from added coal fly ash.

Biochars; biomass-derived charcoal remaining after pyrolysis, have been successfully used to reduce bioavailability and leaching of heavy metals in contaminated soils. Studies revealed that biochar assists in reducing bioavailability of heavy metals through adsorption and chemical transformation, thus helping to control the toxicity of these heavy metals in the soil and in the environment [3]. Under this background the authors hypothesized that co-application of biochar with coal fly ash into Ultisol soils would help attenuate any toxic heavy metal contamination that may occur in soil and ground water due to the application of coal fly ash. The objective of the study was to investigate the effect of biochar on the heavy metal leaching from Ultisol soils amended with coal fly ash, under simulated rainfall conditions.

2. MATERIALS AND METHODS

2.1 Soil, Biochar and Coal Fly Ash

Ultisol soil was collected from a crop field of Georgia (southeastern USA) at a depth of 0–30 cm. The soil was air-dried for 48 h and passed through 2 mm sieve. The initial physicochemical properties; soil structure, particle size distribution, soil pH, EC, organic matter content were determined with respective standard soil testing methods prior to column leaching experiment. Biochar was produced with a locally plentifully available agro waste; avocado branch cut biomass (abundantly available in the region due to hurricanes). The branches were cut to reduce the size and oven dried at 80 °C. Dried biomass was subjected to slow pyrolysis using a furnace (Olympic 1823HE) in a N_2 environment at a temperature of 600 °C for 6 h. After cooling down, biochar was crushed to pass through 2 mm sieve to obtain a uniform size fraction. Class C type coal fly ash collected from a power plant in North Florida was used in the study. They were collected fresh from electrostatic precipitators. Chemical properties and the composition of soil, biochar and coal fly ash are listed in Table 1.

TABLE 1. CHARACTERISTICS OF SOIL, COAL FLY ASH AND BIOCHAR

Property	Soil	Coal fly ash	Biochar
Texture	Sandy	-	-
Density	1.24 gcm^{-3}	-	-
Organic matter %	2.5%	-	-

pH	4.9	11.8	10.3
EC	47.2 µS/cm	6.45mS/cm	34.2 dS/cm
Specific surface area	-	3.9 m^2g^{-1}	610 m^2g^{-1}
C	0.27 %	1.9 %	73.13%
N	0.02 %	0.04 %	0.67 %
S	0.37 %	0.5 %	0.71 %
P	0.01 %	0.01 %	0.09 %
Ca	0.03 %	20.25 %	1.8 %
Fe	6.78 %	7.73 %	2.65 %
Al	8.12 %	27.39 %	0.93 %
Mg	0.02%	2.32 %	4.62 %
K	0.01%	1.15 %	8.25%

The presence of main heavy metals of concern in fly ash were determined by acid digestion of the samples followed by inductively coupled plasma mass spectroscopic (ICPMS) analysis. The results are shown in Table 2.

TABLE 2. HEAVY METAL CONTENT IN FLY ASH (µg/g)

Zn	Pb	As	Ni	Cd	Cr	Se	Mo
263	5.5	21	28	14	96	36	456

2.2. Soil Column Preparation and Incubation

Clear acrylic columns of 16 cm height and 7 cm inner diameter fitted with a bottom plate with 5 mm diameter drainage holes covered with a nylon mesh of 60 µm pore size were used in the experiment. Test columns were prepared with soil only, soil + coal fly ash and soil+coal fly ash+ biochar treatments with triplicates. Columns were packed with soil in layers up to a height of 10 cm, applying weight at each layer to achieve a density of 1.2 g/cm^3. After that, another 5 cm layer was filled with the treatment in which biochar or/and fly ash mixed soil was packed to achieve the same density. Soil amendments mixing rate was 5 tons/ha, based on the column surface area.
A filter paper was placed on top of each column. The columns were wetted uniformly by dipping in a shallow deionized water layer. Capillary rise of water through the soil column was allowed until the filter paper is just wetted. Then, the columns were drained for 24 hours and incubated for 10 days at room temperature.

2.3 Column Leaching Tests and Analysis

Incubated columns were leached by applying a simulated rainfall using a peristaltic pump. Deionized water was applied to the top of the column at the rate of 1.2 mL/min. The leachate was collected at each half pore volume of the soil column, until a total of five pore volumes are collected. This was equivalent to the half a year of rainfall of the area. The leachate fractions were filtered through Whatman 42 (2.5 µm pore size) filter paper and analyzed for the heavy metal concentration using inductively coupled plasma mass spectroscopic (ICP MS) analysis. The leachates collected at each half pore volume and the soil samples collected form the top layer of the column were also tested for pH.

2.4 Statistical Analysis

Differences among treatments and the interaction effect of the treatments were analysed by analysis of variance (ANOVA) statistical technique.

3 RESULTS

The pH of the each treatment layer prior the experiment, after incubation and after leaching is compared in Fig. 1.

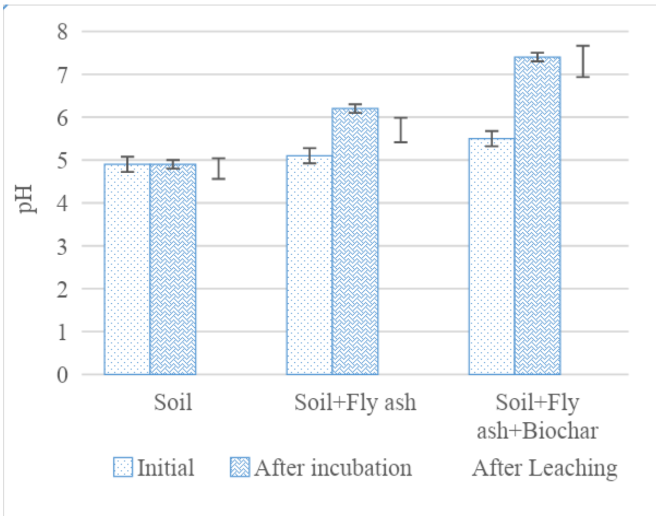
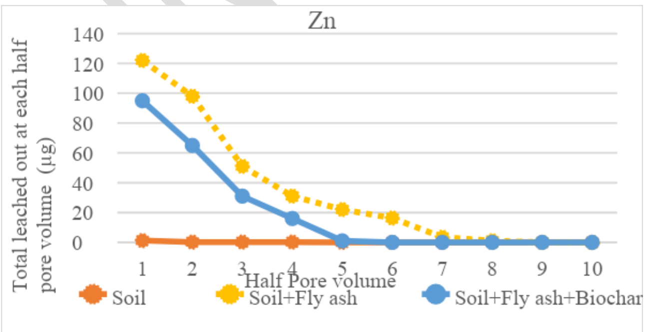
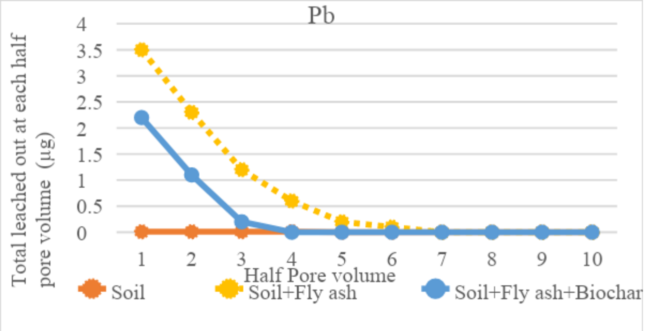
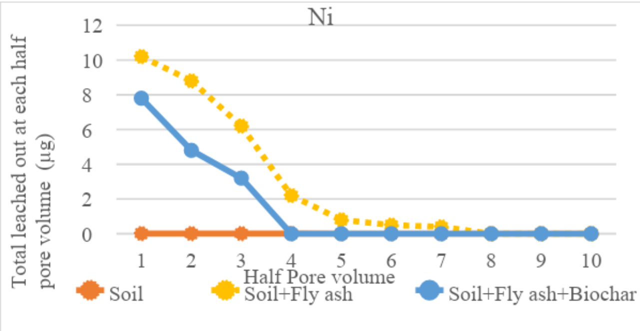


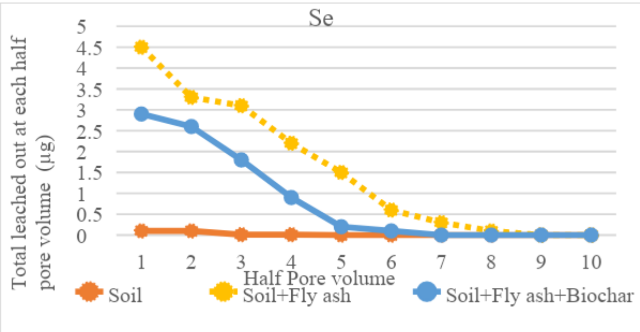
Figure 1: pH of each treatment during different stage of the experiment

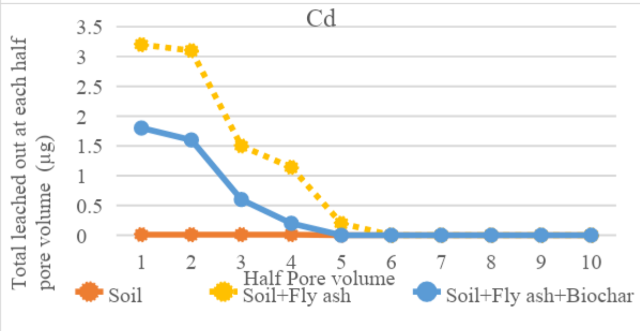
Fig. 2 shows the total of heavy metals leached out at each half pore volume over the leaching event up to a total of 5 pore volumes.




Pb
Total leached out at each half pore volume (µg)
4
3.5
3
2.5
2
1.5
1
0.5
0
1 2 3 4 5 6 7 8 9 10
Half Pore volume
Soil
Soil+Fly ash
Soil+Fly ash+Biochar


Ni
Total leached out at each half pore volume (µg)
12
10
8
6
4
2
0
1 2 3 4 5 6 7 8 9 10
Half Pore volume
Soil
Soil+Fly ash
Soil+Fly ash+Biochar


Se
Total leached out at each half pore volume (µg)
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
1 2 3 4 5 6 7 8 9 10
Half Pore volume
Soil
Soil+Fly ash
Soil+Fly ash+Biochar


Cd
Total leached out at each half pore volume (µg)
3.5
3
2.5
2
1.5
1
0.5
0
1 2 3 4 5 6 7 8 9 10
Half Pore volume
Soil
Soil+Fly ash
Soil+Fly ash+Biochar

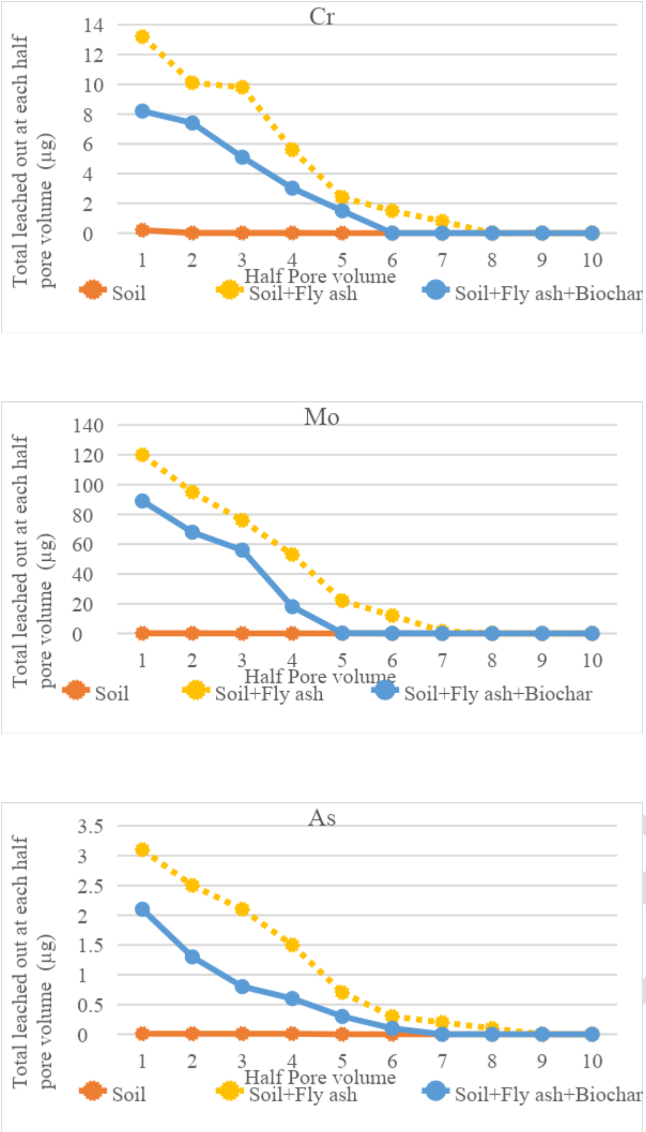


Figure 2: Total metal content of leachate at each half pore volume

4 DISCUSSION

The fly ash and biochar soil amendment with their high alkalinity has significantly modified the the pH of the surface soil layer. The high concentration of K^{+}, Mg^{2+}, and Ca^{2+} content in the biochar form alkaline oxides or carbonates during the pyrolysis process shows liming effect when mixed with soil. Coal fly ash also contains high amount of Ca^{2+} and Mg^{2+}. The alkalinity created by thee ions has increased the pH of the Ultisol soil from strongly acidic range to slightly acidic and neutral ranges after incubation. This suggests that both amendments, coal fly ash and biochar could be good conditioners for acid soils. pH drop observed in all the treatments after leaching compared with values after incubation is attributed to the leaching loss of alkalinity causing metals with the rain water. This loss was greater in fly ash treated soil over fly ash and biochar treated soil. This shows a resistance effect on ion leaching in biochar added soil compared to fly ash only treatment.

Analysis of leachate for heavy metal concentration showed the presence of heavy metals in the leachate collected over five soil pore volumes. The comparison of amount of heavy metals been added to soil initially, (estimated based on the amount of fly ash added and the composition of fly ash), with the cumulative amount of heavy metals leached out, shows up to 50% of leaching trend in some of the heavy metals. Zn, Pd and Ni showed the greatest percentages of leached out. These metals can be considered as the most loosely bound and easily available, of the tested metals in the fly ash matrix.

Biochar addition significantly reduced the leaching trend of heavy metals from soil added with coal fly ash. Leaching reduction rate was 39% for Zn and 55% for Pb, 50% for As, 45% for Ni and 54% for Cd. It was around 41% and 45% for Cr and Se respectively. In heavy metals contaminated soils, the biochar can adsorb and immobilize metal ions due to its porous structure, large surface area, high surface charge density, and pH values [4, 5]. Previous studies have shown the effect of above physicochemical properties of biochars in controlling their effects in soil. Biochar is found to have a net negative surface charge which is more effective at removing cationic species from soil solution than anions. The high surface area (610 m^2g^{-1}) of biochar we observed, suggest a greater potential to sorb abundant positively charged heavy metals added by coal fly ash into the soil.

In addition to the surface charges, the precipitation reactions at elevated pH levels also contributes to reduce the leaching of metal ions from soils added with alkaline soil amendments including biochar and coal fly ash. Chen *et al* (2015) [6] showed that in the presence of biochar Cd precipitates as $Cd(OH)_2$ and Pb likely as $Pb(OH)_2$ when the solution pH is greater than 8. Similarly, biochar application to acidic mine soils raised the pH causing Pb to precipitate as hydroxide phases. Additionally, oxygen containing functional groups present in biochar further enhances positively charged heavy metal iron sorption. Also, workers have observed the conversion of exchangeable Cd and Pb fractions into residual Cd and residual Pb with the addition of biochar into sandy soil which effectively reduces the down migration of heavy metals through the soil profile [7].

Studies also indicated that the effectiveness of biochar in the immobilization of heavy metals strongly depends on the metal contaminant type, the biomass feed stocks used and the pyrolysis conditions [8]. Microstructural level analysis are underway to investigate the mechanism of metal ion retention in Ultisol soils added with coal fly ash and avocado branch cut biochar.

5 CONCLUSIONS

Coal fly ash contains heavy metals that is prone to leach out when added to sandy soil, under subtropical rainfall conditions. Avacado branch cut biochar tested in the study significantly reduced the leaching of heavy metals from coal fly ash in sandy Ultisol. The lachability reduction rates were upto 55%. pH shift in acidic soils after biochar addition, high porosity, high specific surface area and negative surface charges of biochar are believed to be the causes of the metal ion retention. The exact mechanism of metal stabilization is yet to be discovered.

6 DECLARATIONS

Availability of data and materials: Data and materials are available on request.

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