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Characterization of Various Biochar Feed Stocks Enriched with Liquid Fertilizers

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Abstract- Biochar is a porous black carbon material produced through thermochemical reactions in low-oxygen conditions using agricultural and municipal waste materials. Methods such as slow pyrolysis, fast pyrolysis, and hydrothermal carbonization are used. Biochar offers substantial soil benefits, improving its physical, chemical, and biological characteristics. When enriched with liquid fertilizers, biochar becomes a nutrient-rich organic fertilizer solution. Hence the present study was executed with the aims of characterization of various biochar feedstocks enriched with liquid fertilizer. This experiment was conducted as a laboratory experiment at Fruit Crops Research and Development Institute, Kananwila, Horana, Sri Lanka to select the nutrient retention and exchange capacity with different biochar feedstocks. Rice husk, mushroom substrate, banana pseudo stem and coconut shell were used to make the four types of biochar. Ammonium Sulfate, monotassium phosphate, Potassium Chloride, Calcium Chloride, Magnesium Oxide and Zinc Sulfate Fertilizers were used to prepare liquid fertilizer solutions. Initially, 4 types of raw biochar were analyzed for their immediate, chemical, and nutritional elements. Proximate analysis was done as per ASTM D1762-84 method. Banana pseudo-stem biochar showed the best chemical and nutritional results. The nutrient absorbance capacity of each biochar has increased with the concentration of the liquid fertilizer. The nutrient absorbance results obtained from banana pseudo-stem and coconut shell biochar gave the best performances. Further, the study recommended to investigate the nutrient-releasing efficiency of these two biochar types before field applications.

Keywords: Biochar, Nutrient absorption capacity, Nutrient Composition, Proximate and chemical analysis

I. INTRODUCTION

A pyrogenic black carbon material that is porous and produced thermally converting biomass feedstock at low temperatures with little to no oxygen is known as biochar (BC) (Munasinghe et al., 2018). Biochar is often created utilizing a variety of thermo-chemical processes, including slow pyrolysis, fast pyrolysis, hydrothermal carbonization, flash carbonization, torrefaction, and gasification of agronomic waste, such as crop residues, animal farm waste, municipal garbage, and solid waste (Chen et al., 2019). This process results in mass loss due to preferred hydrogen loss as well as volatile carbon loss. The surface area is also larger than the feedstock, especially at the micro-pore scale. In the absence of oxygen, the pyrolysis process can produce biochar from a variety of fuel sources. Numerous physical, chemical, and molecular changes occur during pyrolysis. Volatilization during pyrolysis results in a large loss of mass, which reduces volume and induces shrinkage without significantly altering the feedstock's original structure. (Dejene D & Tilahun E , 2019).

Biochar's basic elements include C, N, H, and a few lower-nutrient elements including K, Ca, Na, and Mg. The ability of biochar to increase cation and anion exchange capacity can be partly credited to its potential to enhance soil fertility, production, and nutritional levels (Sarkhot et al., 2012). Biochar positively influences soil properties, serving as a potent adsorbent to filter pollutants from water. While it enhances soil quality and reduces greenhouse gas emissions, its impact on plant growth varies and requires further study (Sun et al., 2014). According to Sarkhot et al. (2012), applying bio-charcoal in combination with another fertilizer, such as liquid fertilizer, rather than by itself, can boost the effectiveness of the material.

Generally, three procedures are used to improve the production and quality of biochar. Direct treatment entails the direct thermo-chemical conversion of feedstock that is nutrient-rich. Pre-treatment is the process of treating biomass with nutrient-rich ingredients before undergoing thermos-chemical processing to produce high levels of biochar at high pyrolysis temperatures exceeding 600^0C. Biochar is

an excellent soil amendment and fertilizer with a gradual release. It absorbs all nutrients in the soil and they can be released into the soil slowly. Then it acts as a leaching barrier and increases the soil fertility by enriching solutions (Karim et al., 2022). However, it is necessary to identify the quality feedstock available in the vicinity to prepare biochar and the good fertilizer sources to enrich the nutrients into the biochar before field applications.

II. MATERIALS AND METHODS

The Experiment was conducted as a laboratory experiment at Fruit Crops Research and Development Institute, Kananwila, Horana, Sri Lanka.

As the first step, biochar was prepared and as raw materials rice husk, banana pseudo-stem, mushroom substrate and coconut shells were used. Initially, raw samples were collected and small pieces were prepared by cutting and crushing. Then they were filled into the empty crucibles and sealed with crucible lids. Then filled crucibles were placed in a Muffle Furnace and the temperature was adjusted to 50^0C in mins. After each 15 minutes, the temperature was increased by 50^0C until the desired temperature range was completed. Accordingly, 4 types of biochar were prepared from rice husk (50^0C-450^0C), mushroom substrate (50^0C-450^0C), banana pseudo-stems (50^0C-300^0C) and coconut shells (50^0C-1000^0C). After completing the pyrolysis process, the samples were kept to cool down to room temperature before grinding and sieving them for further processing.

During the biochar enrichment process, first, 0.2 g from each biochar sample was measured and transferred to a 100 mL conical flask and 50 mL of liquid nutrient solution was added to the conical flask. Seven different concentrations of liquid solution were used for the treatments; 20 ppm, 40 ppm, 60 ppm, 80 ppm, 100 ppm, and 120 ppm and distilled water was used for the control. Duplicate samples were obtained from each biochar. All prepared conical flasks were then placed on a shaker at 200 rpm and kept for one day (24 hours) for incubation and enrichment. After 24 hours, the shaken samples were filtered using filter papers and stored at room temperature.

Then, 8 mL of HNO3 and 2 mL of H202 were added into each vessel and they were fixed into the digestive units. This process was done in a Fume Hood. Finally, the SK 3150 program was run. When the program was running the door was auto-locked and after completing the program, the door was unlocked. During the program, sample storing bottles were prepared by cleaning them from heated de-ionized water. Then, the vessels were removed from the digestive unit and kept for a few minutes to remove the fume in a fume hood. Then the filtrate was collected into 100 mL measuring cylinders and they were topped up into 50 mL using distilled water.

A. Proximate analysis

American Society for Testing and Materials (ASTM) D1762-84 method was followed for the determination of moisture, volatile matters and ash content.

1) Moisture content

Moisture content was determined by using the standard oven-dry method (Aller et al., 2017). First, the Muffle Furnace was heated up with the empty crucibles and lids for 10 minutes. After that, crucibles were placed in desiccators for 1 hour. After the crucibles were ready, approximately 1 g of the sample was put into the crucibles covered with lids and placed in the Oven (105 0C) for 2 hours. Dried samples were placed in the desiccators for 1 hour and weighed. Duplicate samples were obtained from each biochar. The moisture content was determined from the difference between air-dried samples and oven-dried samples.

$$\text{Moisture } \% = \frac{A-B}{B} \times 100$$ Eq; 01 (Aller *et al*., 2017)

Where

A = Grams of air-dried samples

B = Grams of oven- dried samples at 105 ^{0}C

2*) Volatile matter content*

To determine the volatile matters, first Muffle Furnace was heated up to 950 0C. And preheated samples for moisture determination were placed when the furnace door opened, for 2 min for the outer edge of the furnace at 300 0C and 3 min for the edge at 500 0C. Then samples were placed in the Muffle Furnace for 6 minutes closed the door. Then samples were placed in desiccators for 1 hour and weighed (Aller et al., 2017).

$$\text{Volatile matter } \% = \frac{B-C}{B} \times 100$$ Eq:02 (Aller et al., 2017)

Where,

C = Grams of samples after drying at 950^0C

3) Ash content

The samples used for volatile matter determination were uncovered and crucibles were placed in the Muffle Furnace at 750^0C for 6 hours, then they were transferred into desiccators for cooling and weighed to determine the ash content.

$$\text{Ash } \% = \frac{D}{B} \times 100$$ Eq: 03 (Aller et al., 2017)

Where,

D = Grams of residues

B. Chemical parameter analysis

1) pH value

pH of biochar was measured by an electric pH meter. Duplicate samples were prepared in a 1:10 ratio (biochar: distilled water), and samples were shaken in an Electric Shaker for 30 minutes at 180 rpm. Next, shaken samples were equilibrated for 1 hour for settled biochar. First, the pH meter was calibrated from the pH

buffers, such as 4, 7 and 10. After that H+ electrode was placed into the settled sample to get the values (Singh et al., 2017).

2) EC value

EC was measured in 1:10 diluted biochar samples from a calibrated Electric conductivity meter.

Total element analysis

In total element analysis, N, P, K, Ca, Zn, and Mg of biochar samples were analyzed. Nitrogen level was determined by using the Kjeldhal method. Available Phosphorous was measured by using the Olsen method in a Spectrophotometer. K and Ca were checked from the Flame Photometer. Also, Atomic Adsorption Spectrophotometer was used to calculate Zn and Mg (Singh et al., 2017).

3) Cation Exchange Capacity

Ammonium Acetate, Ethyl alcohol (95%), Hydrochloric acid, Boric acid solution, Sodium Hydroxide (40% solution, Mixed indicators (0.1 g of Bromocresol Green and 0.02 g of Methyl Red indicators in 100 mL of 95% Ethyl alcohol) were used as reagents of the cation exchange test. 10 g of biochar was weighed into the extraction bottle and 50 mL of Ammonium Acetate solution was added into the bottle. Next, it was placed on the Mechanical Shaker for 30 minutes. The biochar suspension was transferred into a Buchner Funnel fitted with No. 42 filter paper. Then the leach-out sample was washed with an excess of 150 to 200 mL of Ammonium Acetate. Then filtrate was collected into a 1 L flask.

The excess Ammonium Acetate from the biochar samples was washed with 150 to 200 mL Ethyl alcohol (95%) and the filtrate was discarded. It was changed to a 1 L receiving flask and biochar samples were washed with 250 mL of 0.1N HCl to replace the exchangeable ammonium.

The filtrate was transferred to an 800 mL Kjeldahl flask. And 10 g of NaCl, 30 mL of 40% NaOH, and an anti-bumping disc were added into the flask. The flask was placed in the Kjeldahl distillation unit. Approximately one-third of the distil solutions were added into a 500 ml receiving flask,50 mL of saturated boric acid solution and three drops of mixed indicator. The solution was titrated with 0.1N HCL, and the cation exchange capacity (CEC) in meq per 100 g of biochar by using the below equation. (Roberts et al., 1978).

$$\textit{CEC in meq per 100g of biochar} = \frac{\textit{l of HCl} \times \textit{N of HCl}}{\textit{10 g of sample}} \times 100 \quad \text{(Eq: 04)}$$

c.

The various biochar feedstocks enriched with liquid fertilizer were compared using a one-way analysis of variance (ANOVA) followed by Turkeys' post hoc test at a 5% significant level.

II. RESULTS AND DISCUSSION

A. Proximate analysis of raw biochar

According to the results of raw biochar proximate analysis, shown in Table 1, significant. Nutrient absorption capacity of various biochar

Table 1: Proximate analysis of raw biochar samples

Types of bio char	Mean ± SD		
	Moisture %	Volatile Matter %	Ash %
Rice Husk	6.78 ± 0.01^{b}	15.39 ± 1.26^{b}	47.46 ± 0.08^{a}
Mushroom Substrate	6.09 ± 0.09^{bc}	28.11± 0.72^{ab}	33.47 ± 0.28^{b}
Banana Pseudo-stem	8.24 ± 0.46^{a}	42.95 ± 8.97^{a}	17.08 ± 2.62^{c}
Coconut Shell	5.15 ± 0.05^{c}	14.29 ± 1.20^{b}	2.11± 0.00^{d}
Grand Mean	6.56	25.18	25.03
P	0.003*	0.033*	0.001*
CV %	18.76	52.97	73.05

Values indicate mean ± standard deviation (SD) (Percentage) and different letters show significant differences at a 5% significant level.

1. Moisture Content

Statistical analysis of the moisture content data indicated significant (P = 0.003) differences among 4 biochar types. The highest moisture content is in banana pseudo-stem biochar (8.24%) and the lowest was observed in coconut shell biochar (5.15%). When considering the characteristics of the pure biomass samples, the high level of moisture content may be from the fibrous nature of the banana pseudo-stem. Banana pseudo stem is naturally lignocelluloses. It contains a high level of lignin and a low level of cellulose. Then it has made the porous structure for favouring the absorption of a high percentage of moisture by the microporous of the banana biochar (Sarkar & Wang, 2020). The reported low moisture content in coconut shell biochar, proves that the

coconut shell contains more cellulose than lignin which causes for low moisture.

2) Volatile matter percentage

According to literature (Abdullah et al., 2014), banana pseudo-stem has lower carbon and hydrogen content but high sulfur, nitrogen and oxygen content. When a material has high oxygen content, this would indicate a high volatile content. Other biochar types made from mushroom substrate (28.11%), rice husk (15.39%) and coconut shell (14.29%) have a lower concentration of volatile components than the banana pseudo-stem biochar (42.95%).

4) Ash percentage

Rice husk biochar had the highest ash content (47.46%), followed by mushroom substrate (33.47%). Rice husks are unusually ash-rich; further research (Leksungnoen P et al., 2019) found that high levels of Silicon in rice plants are closely correlated with the high ash content of rice husk biochar.

Pyrolysis was mainly influenced by the feedstock and to a lesser extent by the pyrolysis temperature. That could be why the rice husk biochar has significantly higher ash content than others. Similarly mushroom substrate biochar has high ash content due to its high Zinc content. In the production of mushroom substrates, grain flours are used for nutrient enrichment, mostly rice bran. It contains more Zinc (33 ppm), in mushroom seed production paddy rice is the medium for mushroom growth and rice husks are used for media preparation (Chae & Ahn, 2013). This can be the case with an increase in the high level of Zinc. Others, however, were not rated highly.

B. Chemical Analysis

Values indicates mean ± standard deviation (SD) (Percentage) and different letters show significant different differences at 5% significant level.

According to the presented data in Table 2, there is a significant difference at $p \leq 0.05$ for tested chemical parameters such as, Electrical Conductivity (EC) and pH value of the 4 types of biochar. According to that results banana pseudo-stem biochar has high EC (9060.00 µS/cm). The EC is comparatively high in mushroom substrate biochar, which contains more lignin. Coconut shell biochar indicated the lowest EC (445.50 µS/cm).

pH of the biochar is situated in wide range such as 4.6 to 9.3. Coconut shell biochar had the highest alkaline pH (9.31), whereas banana pseudo-stem (7.26) and mushroom substrate (7.90) had neutral pH ranges. But rice husk biochar has a slightly acidic pH (5.66).

Table 2: Chemical parameters of biochar samples

Types of Biochar	Mean±SD	
	EC (µS/cm)	pH
Rice Husk	737.00±1.00^{c}	5.66±0.02^{d}
Mushroom Substrate	3500.00±20.00^{b}	7.90±0.06^{b}
Banana Pseudo-stem	9060.00±330.00^{a}	7.26±0.04^{c}
Coconut Shell	445.50±4.50^{c}	9.31±0.05^{a}
Grand Mean	3435.63	7.53
P	0.001*	0.001*
CV %	107.76	18.65

C. Nutrient composition of various biochar types

The present study (Table 3) revealed that, there are different nutrient concentrations in each of the four types of biochar. Nitrogen concentration of rice husk biochar, mushroom substrate biochar, banana pseudo-stem biochar and coconut shell biochar are 2296, 336, 2856 and 1120 mg/L respectively and those are not significantly different.

Although rice husk biochar has the highest Nitrogen, banana pseudo-stem biochar also has higher nitrogen content than the others due to its more lignin percentage according to Biswas et al. (2021).

In addition, a high, Concentration of Zinc and Phosphorus were found in the mushroom substrate (147.05 and 758.66 mg/L respectively). Because it contains Zinc and Phosphorous rich materials such as cereal flours and rice bran. Among the three types, banana pseudo-stem has the highest K levels (40000 mg/L).

Additionally, a high amount of Magnesium was found in Coconut shell biochar (121.99 mg/L). Further 4 types of biochar had significant differences in Potassium (0.0001*) Calcium (0.0001*) and Zinc (0.003*) contents. Phosphorus and Magnesium contents had no significant differences.

Table 3: Nutrient composition of various biochar types

	Mean ± SD					
	N (mg/L)	**P(mg/L)**	**K (mg/L)**	**Ca (mg/L)**	**Mg (mg/L)**	**Zn (mg/L)**
Rice Husk Biochar	2296 ± 0.00	221.81 ± 7.2[a]	9037.5 ± 137.0[b]	63625 ± 2125.0[b]	91.5 ± 0.75[a]	37.84 ± 1.74[b]
Mushroom Substrate Biochar	336 ± 0.00	758.66 ± 586.17[a]	5425 ± 75.00[c]	89625 ± 625.00[a]	5.18 ± 0.68[a]	147.05 ± 157[a].
Banana Pseudo-stem Biochar	2856±0.00	164.77±37.92[a]	40000±0.00[a]	20312.5±9370[d].	74.25 ± 39.75[a]	37.98 ± 7.08[b]
Coconut Shell Biochar	1120 ± 0.00	132.89 ± 108.7[a]	4462.5 ± 87.5[d]	37250 ± 1250.0[c]	121.99 ± 26.0[a]	23.05 ± 9.68[b]
Grand Mean	1652.00	319.53	14731.25	52703.13	73.23	61.48
P value	-	0.487	0.0001*	0.0001*	0.095	0.003*
CV%	63.73	131.51	106.59	53.45	71.53	88.26

D. Biochar Enrichment

Table 4: Nutrient absorption capacity of various biochar types at 80 ppm

	Treatments (Mean±SD)					
	N value	**P Value**	**K Value**	**Ca Value**	**Mg Value**	**Zn Value**
Rice Husk Biochar	48.99±0.40[c]	69.5933±0.14[b]	67.2550±00806[b]	56.2208±10.063[d]	69.96±0.626[a]	69.9817±0.024[b]
Mushroom Substrate Biochar	48.29±0.404[c]	69.5333±0.1422[c]	66.9458±0.00806[c]	57.9125±10.063[c]	67.94±0.626[b]	69.9967±0.024[a]
Banana Pseudo-stem Biochar	55.99±0.404[a]	69.5808±0.1422[b]	59.9792±0.00806[d]	66.8767±10.063[a]	66.49±0.626[b]	69.9583±0.024[d]
Coconut Shell Biochar	52.03±0.404[b]	69.6492±0.1422[a]	67.4592±0.00806[a]	65.3583±10.063[b]	62.13±0.626[c]	69.8592±0.024[d]
P value	0.000*	0.000*	0.000*	0.000*	0.000*	0.000*

According to the data shown in Table 4 at the 80ppm level, significant differences (0.000*) were found at $p \leq 0.05$ for all the observed nutrient absorbance. The structures of the tested four types of biochar have changed according to the natural biomass type. A high level of moisture present in banana pseudostem biochar is due to its high porosity. Because of that high porosity, it can absorb more nutrient elements and its performance becomes better. According to the results, banana pseudo-stem biochar has absorbed more N and Ca levels from the liquid fertilizer solutions. Similarly, it has absorbed the other liquid fertilizer solutions in high ranges as well. When considering the coconut shell, it contains a low level of nutritional level in pure one but it has high absorption performances for P and K. Therefore the highest P (69.6492) and K (67.4592) absorber was coconut shell biochar. BC (Banana pseudostem biochar) and RC (Rice husk biochar) biochar were shown the same absorbance rate (69) of Phosphorous absorption because of the high level of Nitrogen content present in their pure char samples. The highest Mg and Zn absorbers were rice husk biochar and mushroom substrate biochar respectively.

III. CONCLUSION

Based on the results of the present investigation, banana pseudo-stem biochar shows the best nutrient content as a raw material for producing biochar among the tested 4 biochar types. However, according to the results obtained in biochar enrichment, the absorption of liquid fertilizer has changed depending on the type of biochar. The absorbance capacity of each biochar has increased with the concentration of the liquid fertilizer, showing higher absorbance at higher concentrations and lower absorbance at lower concentrations. Among the 4 types, coconut shell biochar and banana pseudo-stem biochar show higher absorption rates than the other two biochar types. According to the results of this experiment, enriched coconut shell biochar and banana pseudo-stem biochar can be prescribed as improved fertilizers for farmers. However, before recommending them to the farmers for field applications, it would be better to study the nutrient-releasing efficiency of these two biochar types.

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