RESEARCH ARTICLE

NUTRIENT CONTENT AND MORPHOLOGICAL CHARACTERISTICS OF FEW WASTE DERIVED SLOW PYROLYZED BIOCHARS

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Abstract

Five(5) different waste-derived biochar viz. animal bone, corn stover, wood chips, green coconut palms, and nutshells were slow pyrolyzed (500±50°C) and further investigated to know their morphological characteristics and nutrient contents. Results produced the fact that corn stover biochar had the best nutrient status along with excellent physical properties like water holding capacity (525%) and CEC (251.85 Cmol/kg) whilst coconut palm biochar was the second-best among all categories. The average particle size of WC biochar 0.82 (μm²) was the largest along with the maximum pore depth. Nonetheless, the region of this biochar was occupied by remarkably small particles, which was 47.42%. The corn stover biochar, on the other hand, had the smallest average particle size (0.18 μm²) and the lowest particle area (9.19%). WC biochar (51.3%) and CS biochar (46.2%) had the highest organic C value, while biochar nutshell had the lowest (15.31%), sequentially. Nutrient content can vary depending on the variation in the feedstock mostly N, P, K, and S in total content. Animal Bone biochar (3.89 percent) and biochar nutshell (3.32 percent) exhibited the highest total N content. In the interpretation, high phosphorus concentrations resulted in biochar derived from animal bone feedstock (8.44%), whereas other biochars were less than 1%. The CP biochar had higher total K content than other biochars. All the biochars exhibited equal total S concentration other than biochar derived from the animal bone (2.34%) had a higher percentage of total K compared with other biochar. Biochar related wastes showed a very low concentration of heavy metals such as Cr, Pb, Cd, and Ni. The overall amount of lead and cadmium in all of the biochar was below the detection mark.

Introduction:

Biochar (BC) is a carbon-rich product produced when biomass, such as wood, manure, or leaves, is heated in a closed container with little to no available air. BC is a compact carbonaceous substance that is generated from heating biomass at or above 250 °C in the absence of limited air. It was originally planned for use in sequestration of carbon (C) and soil amendment but has now extended toward environmental management (Lehmann and Joseph

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Biochar's history is correlated with the discovery of "Terra Preta di Indio" (also called Amazonian Dark Earths) in Amazonia, where the dark earth soils (accounting for * 10 percent of Amazonia) were formulated using the slash-and-char technique by the slow-moving addition of biochar (Laird et al 2009).

For hundreds to thousands of years, the dark earth soils persevered high fertilities (Wiedner et al. 2015). This discovery triggered scientists to intentionally produce biochar using modern artificial techniques to recreate the ancient agricultural miracle in Amazonia. Biochar feedstock includes assorted biomasses, especially waste and low-value biomass such as agricultural straw, livestock manure, wood chips, and sawdust (Shaheen et al 2019). Thus, the development of biochar will complete the resource utilization purpose of this biomass waste, a value-added process. Besides, during biochar processing, by-products such as bio-oil and syngas can be solicited and utilized as bioenergy (Liu et al. 2017). BC has a broad specific surface area, a porous structure with an abundance of available surface groups and can be used as a sorbent or passivator to remove or immobilize inorganic and organic pollutants from water or soil (Zheng et al. 2019; Yuan et al. 2019; Liu et al. 2018; O'Connor et al. 2018). Because of these advantages, such as improving soil quality, reducing climate change, mitigating greenhouse gas (GHG) emissions (e.g. CO2, CH4, and N2O), remediating water and soil pollution, managing and using waste biomass, and generating bioenergy (e.g. bio-oil, syngas), biochar technology has attracted public interest in the past decade (Shen et al. 2015; Abiven et al. 2015). Newly, increasing studies have suggested biochar beyond soil enhancement and sequestration as a management accessory to connect environmental safeguard and bioenergy improvement (Yuan et al. 2019; Xiao et al. 2018; O'Connor et al. 2018).

The new notion of field application is still distinct, with only a few research activities being conducted here in Bangladesh. In this study, it was being concentrated on the biochar made from various waste materials such as stolid bone, maze things, wood chips, green coconut palm, and nutsheells. This analysis work will, therefore, be carried out to use waste as a feedstock concerning the production of biochars and comparing its characteristics with each other and it will serve as a waste management process in the future.

Materials and Methods:-

Feedstock Selection
Ten different types of wastes were collected to produce different types of biochar. All the feedstock selected are potentially waste materials, and collected from different sources. Animal bones (Fish, Chicken, Cow, and Goat) collected from the meat market in Malibagh Bazar, home leftover, and leftover after the Eid festival (Eid-ul-Azhar).

Corn Stovers were collected from Sher-e-Bangla Agriculture University. Wood Chips were collected from sawmill (Rahim Timber and Saw Mill) from Abu Hotel, Chawdhury Para, Dhaka. Sewage Sludge was collected from Pagla Sewage Treatment Plant. Sugarcane bagasse was collected from the roadside sugarcane juice shop. Green Coconut palm collected from the coconut market near Malibagh Bazar. Nutshells were collected from the peanut shop near Wari Bazar. Potato peels were arranged from the small agro-food processing industry in Puran Dhaka. Water hyacinths were collected from a pond, located in Keraniganj, Dhaka. Organic Wastes were collected from home leftover vegetables and other municipal wastes.

After collection, the materials were packed in polythene bags, and the bags were tied with strings to prevent any air-exchange between the atmosphere and the sample itself. The bags were labeled with markings of date, name of collection site, name of collector, etc.

Processing and Production of Biochar
Until biochar was processed, all the waste derived feedstocks were dried warmly under sunlight for a few days. When all the feedstocks had been fully dried, all the feedstocks were processed one by one and pyrolysis was performed in a specially built kiln. Initially, a pressure cooker was gathered from a old Dhaka recycling store. Then it was set, and the upper part of the cooker is connected to a stainless steel screw and a pipe. The entire pressure cooker was tightened to the air by using a heat resistance rubber in the cooker's head. The pipe was used to cut the cooker generating syngas.

Individual feedstocks were arranged in the bally of the cooker and then the head of the cooker is locked that no oxygen can enter inside the cooker. The cooker was then placed on the gas stover for burning. After one hour of burning, an approximate temperature 450-550ºC was maintained. The feedstock was roasted for 3 hours to maintain the above-mentioned temperature. After the completion of the process, the cooker was removed from the gas stover.
and it was kept for 2 hours to cool down. The head of the cooker was not opened because it can readily be oxidized in contact with atmospheric air. After the biochar cooled down, the lid of pot opened and screened through a 0.25mm stainless sieve and then kept in plastic jars with paper tags indicating source, manufacturing date etc.

**Table 1:** Types of waste used to produce biochar and symbols.

| Waste used for Biochar Production | Biochar Symbols |
|----------------------------------|----------------|
| Animal Bone                      | AB             |
| Corn Stover                      | CS             |
| Wood Chips                       | WC             |
| Coconut Palm                     | CP             |
| Nutshells                        | NS             |

**Laboratory analysis and analytical procedure**

To determine the water holding capacity by mass ASTM (2010) method was followed. The morphological properties of biochars were analyzed by Scanning Electron Microscopic (SEM) imaging. A range of SEM images (Magnification: 2000× to 10,000×) was captured with a JEOL JSM-6490 operating at 20KV at the Center for Advanced Research in Sciences (CARS), University of Dhaka. Image analysis was done with ImageJ version 2.0 with appropriate threshold and size range values.

The pH, electrical conductivity (1: 10 ratio), and cation exchange capacity (CEC) of biochar samples were measured as described in Rayment and Higginson (1992). Organic carbon of the feedstock and biochar was determined by the wet oxidation method of Walkley and Black (1934). Total N of the samples was determined by the Kjeldahl steam distillation method (Jackson 1962). The concentration of P, K, and S in feedstocks and biochars were analyzed after digestion with nitric-perchloric acid (Jackson 1962). Total P was measured colorimetrically using a spectrophotometer by developing yellow color with vanadomolybdate, total K by flame photometer, and total S by the turbidimetric method using a spectrophotometer (Jackson 1962).

Statistical analyses were done by using Minitab 19.

**Results and Discussion:**

**Physical and Morphological characteristics of biochars**

It is now generally accepted that modern agriculture heavily relies on chemical fertilizers and artificial irrigation. In many regions, inappropriate land management activities have led to unproductive sandy soils with a decreased capacity to hold water. The corn stover biochar possessed the highest water retention of 525% that is nearly ten times more than that of animal bone biochar, which may be due to increased porosity of corn stover (Table 2). Both wood chip biochar and coconut palm biochar also have high percentage of water holding capacity. On the other hand, animal bone biochar (67%) has very low water holding capacity than other biochars. Biochar could be a competent amendment to light soils especially for newly developed lands with high sand deposited, as provides high water holding capacity (Piash et al., 2016).

**Table 2:** Water holding capacity, particle size and area occupied by particles in different waste derived biochars.

| Properties                  | Biochar Types |
|-----------------------------|---------------|
|                             | AB  | CS  | WC  | CP  | NS  |
| Water Holding Capacity (%)  | 67  | 525 | 218 | 246 | 192 |
| ±2.3                        | ±3.1| ±7.5| ±2.0| ±4.1|
| Particle size (μm²)         | 0.25 | 0.18 | 0.82 | 0.32 | 0.21 |
| ±0.07                       | ±0.02| ±0.06| ±0.05| ±0.02|
| Area covered by particles (%)| 18.11 | 9.19 | 47.42 | 44.97 | 26.24 |
| ±0.05                       | ±0.07| ±0.17| ±0.31| ±0.23|

'±' Standard Deviation

Improving biochar performance, selection of feedstock, and conditions of manufacture requires a comprehensive understanding of structure and particle distribution. Typically, biochars consist of abundant minerals and organic structures. The structural composition of the surface morphology of all the biochar materials was highly diverse. Here are some Figure of SEM image analyses with 5000 times zoom.
After analyzing the images with ImageJ software (Table 2 and Fig. 1) wood chips biochar's average particle size 0.82 (μm) was the biggest along with its highest pore volume (Fig. 1). However, this biochar’s area occupied by particles in surprisingly high which is 47.42%. In contrast, corn stover biochar possessed the smallest average
particle size (0.18 μm²) and lowest area occupied by particles (9.19 %). These biochars' highly spongy and honeycomb-like porosity can provide a high surface area that, when incorporated into the soil, is likely to increase soil aeration, water holding capacity, and nutrient retention.

**Chemical characteristics of biochars**

Most of the biochar found to be alkaline in nature (pH 6.4 to 10.02) due to high dissolution of base cations (Table 3). Because of the production methods and the high temperature, the pH value of biochars increases, probably due to the relative concentration of non-pyrolyzed inorganic elements already present in the original feedstocks (Cantrell et al., 2012).

**Table 3:** Chemical properties of biochars such as, pH, and EC (mS/cm).

| Parameters | AB | CS | WC | CP | NS |
|------------|----|----|----|----|----|
| pH         | 6.82 | 7.17 | 6.49 | 8.20 | 7.77 |
| EC         | 1.13 | 1.27 | 0.05 | 2.22 | 0.13 |

The alkaline properties of Biochar can be specified in four broad divisions: surface organic functional groups, carbonates, soluble organic compounds, and another inorganic alkali including oxides, hydroxides, sulfates, sulfides, and orthophosphates (Cheah et al., 2014). Increased pH of biochar modified acid soils can help decrease Al-toxicity and increase availability of P.

Electrical conductivity was very high for biochars produced from young coconut palm (2.22 mS/cm) and in animal bone and corn stover EC value is moderate (Table 3). Other biochars had relatively lower EC. High EC results may be due to the high concentrations of soluble salts.

![CEC (Cmol/kg)](image)

**Fig. 2:** Cation Exchange Capacity (CEC) of waste derived biochars.

Cation exchange capacity (CEC) refers to the biochar's ability to hold cationic nutrients. Soils with high CEC values can hold cationic fertilizers (K⁺ and NH₄⁺) in the root zone and prevent leaching of the nutrients. The CS biochar showed highest CEC (251.85 Cmol/kg) (Fig. 2) which is almost sixteen times of the most mineral soils (≤15 Cmol/kg) indicated this biochar could be an interesting soil amendment for sandy soils (Usowicz and Lipiec, 2017). Animal bone biochar had the lowest CEC that is 25.65 Cmol/kg followed by nutshells biochar (96.6 Cmol/kg) (Fig. 2). Meszaros et al. (2007) anticipated that K, Ca, Mg, Na and P in biomass promote the formation during pyrolysis of O-containing groups on the biochar surface, resulting in higher CEC. Biochars with elevated CEC may also be an option for environmental management to remediate heavily metal contaminated soil or water (Koutcheiko et al., 2007).
Carbon content and nutrient status of biochar

Results indicated that wood chips biochar (51.3%) and corn stover biochar (46.2%) possessed the highest organic C content, respectively whereas nutshells biochar holds the lowest (15.31%) (Table 4). This stable form of organic C would greatly influence soil physicochemical properties.

High-temperature biochar exhibits a high degree of degradation-resistant aromatic C structures, as they do not provide a labile fraction of C to soil microbes (Novak et al., 2009). Biochar is commonly considered comparatively inactive as compared to its feedstocks. Biochar carbon appears to be present in soils, depending on the feedstock and type of pyrolysis, for hundreds to thousands of years (Grutzmacher et al., 2018).

Table 4: Total Organic Carbon (OC) in Biochars.

| Parameter | Biochar Type |
|-----------|--------------|
|           | AB | CS | WC | CP | NS |
| OC (%)    | 18.0±1.9 | 46.2±1.8 | 51.3±2.34 | 28.0±1.02 | 15.31±1.76 |

‘±’ standard deviation

The improvement in soil C and nutrient status is due to thermal humiliation which indicates the loss of volatile compounds (mainly H and O) from the original material and relatively small volatilization losses of alkaline nutrients (White and Krstic, 2019).

Pyrolysis reconstructs the nutrient content in the resulting biochar, thus affecting plant nutrient availability. Nutrient content can diversify depending on the variation in the feedstock mostly N, P, K, and S in total content. Animal bone biochar (3.89%) and nutshells biochar (3.32%) had the highest content of total N (Table 5). Total N contents of biochar, produced from potato peel, water hyacinth and organic matter had around 3 ppm that was much higher than remaining biochar.

Table 5: Total nutrient status (%) of biochars.

| Nutrients | Biochar Types |
|-----------|--------------|
|           | AB | CS | WC | CP | NS |
| N         | 3.86±0.22 | 0.74±0.07 | 0.36±0.01 | 1.20±0.12 | 3.32±0.14 |
| P         | 8.44±0.09 | 0.10±0.02 | 0.04±0.01 | 0.13±0.03 | 0.02±0.01 |
| K         | 0.20±0.03 | 0.94±0.04 | 0.14±0.07 | 2.20±0.07 | 0.58±0.04 |
| S         | 2.34±0.08 | 0.61±0.09 | 0.64±0.04 | 0.41±0.04 | 0.68±0.09 |

‘±’ Standard Deviation

Essentially the influence of feedstock is especially manifest in the case of total P. In the research, a high concentration of phosphorus resulted in biochar produced from a feedstock of animal bone (8.44%) whereas other biochars like wood chips and nutshells waste recorded lower than 1%. CP biochar had higher total K content than other biochars. All the biochars showed a similar concentration of total S other than biochar produced from animal bone (2.34%) had a higher percentage of total K than other biochar.

Biochars are variable materials in terms of total nutrient content, and the availability of nutrients may vary according to plant and soil response. Accessible nutrient content is a big factor for plant growth. In Fig. 3, available N, P, K and S in the biochars varied according to the feedstock. Available N content is found in most biochars, too. Biochars are generally very low in N- that is, Nitrate-N, and Ammonium-N mineral forms. The effects of the type of feedstock and its conversion processes on the speciation of biochar availability of P and K is still not well understood.
In this case, the pyrolysis process of biochar production also plays an important role. Because of the same reason, a smaller amount of P is generally lost than C or N as it transforms into less soluble minerals resulting in a reduction of the available P in biochars (Zheng et al., 2013). Available sulfur content in biochar alternate depending on biochar production methods like pyrolysis or gasification (>700°C). Pyrolyzed waste showed result of available sulfur content below 1% (Fig. 3).

Other macro and micro nutrient status biochar
The total sodium content of most of the biochar were low in concentration (Table 6). Animal bone biochar had the maximum Na content (0.62%), which was almost triple than that of corn stover biochar (0.04%).

Table 6: Total macro and micro nutrient status of biochars.

| Nutrients | Biochar Types |
|-----------|---------------|
|           | AB | CS | WC | CP | NS |
| Na (%)    | 0.62 | 0.04 | 0.07 | 0.30 | 0.09 |
| Ca (%)    | 0.33 | 0.05 | 0.004 | 0.006 | 0.001 |
| Mg (%)    | 0.014 | 0.018 | 0.006 | 0.0064 | 0.0012 |
| Fe (mg kg⁻¹) | 2.17 | 7.9 | 6.6 | 14.6 | 7.3 |
| Zn (mg kg⁻¹) | 1.12 | 0.55 | 0.44 | 0.48 | 0.43 |
| Cu (mg kg⁻¹) | 0.032 | 0.026 | 0.048 | 0.138 | BDL |

BDL - Below Detection Limit

Soluble Na attributed for the higher EC in soil. The high EC of the analyzed biochar might be the reason of huge Na content. Same as Na content, AB biochar had highest amount of Ca content (0.33%), as animal bone feedstock contain mostly calcium. Corn stover biochar had the second highest Ca content. In contrast, Mg contents found low in all the biochars. High production temperatures resulted in biochar depleting decomposable substances, volatile compounds, and elements such as O, H, N, S, and, as a result, enhanced concentrations of other essential nutrients, including Ca, Mg, etc. (Kim et al., 2012). Total Fe content of CP biochar was high (14.6%) while with 2.17% animal bone biochar had the lowest amount of iron. Biochar demonstrated a slight variation in total Zn content ranged from 0.43 to 1.12 mg kg⁻¹. The highest amount of Zn found in AB biochar (1.12 mg kg⁻¹) but it was very
lower (1350 to 2175 mg kg$^{-1}$) than the previous studies reports (Hossain et al., 2011). Most of the biochar resulted in low amount of copper content. Nutshell biochar had below detection limit in terms of total copper content.

**Heavy metals status of biochar**

Total chloride content of the biochar was ranging from 30 – 4900 ppm (Table 7). Corn stover biochar (4900 ppm) and animal bone biochar (3900 ppm) had high amount of chloride content; in contrast, nutshell biochar had the lowest (30 ppm) chloride content.

**Table 7:** Heavy metal status (ppm) of biochars.

| Elements | AB   | CS   | WC   | CP   | NS   |
|----------|------|------|------|------|------|
| Cl       | 3900 | 4900 | 1100 | 1200 | 30   |
| Cr       | 0.091| 0.088| 0.097| 0.061| 0.129|
| Pb       | BDL  | BDL  | 0.14 | BDL  | 0.08 |
| Cd       | 0.002| 0.001| 0.001| 0.001| ND   |
| Ni       | 0.02 | 0.03 | 0.01 | 0.04 | 0.06 |

BDL- Below Detection Limit

Biochars have heavy metals fixed in their structure, derived from their source material, which may have accumulated and combined in ash fractions during pyrolysis (Lehmann and Joseph, 2015). Waste derived biochar demonstrated very low concentration of heavy metals like Cr, Pb, Cd and Ni (Table 7). Highest amount of chromium resulted in NS biochar (0.129 ppm). Both animal bone biochar and wood chip biochar had similar concentration of total chromium. Total lead content and cadmium content in all the biochar were below detection limit. In contrast, nutshells biochar was containing high amount of nickel (0.06 ppm) than other biochars.

**Conclusion:**

Waste derived biochars displayed varying physicochemical properties and nutrient content. The water hyacinth biochar exhibited high surface area, water keeping, and cation exchangeability while the biochar of domestic organic waste had increased the critical nutrient content. As a result, feedstocks for biochar production must be carefully selected to meet the needs of a specific combination of soil and crops. The biochars adopted in this research are readily available and some have a high potential to be practiced in the agricultural system. Nevertheless, the cost-benefit ratio, the production cycle, the production temperature effect, and socio-economic factors should be analyzed before implementation on the soil. Depending on their material origin and production conditions, BC's characteristics and the heavy metal content themselves alter considerably. They have different consequences on heavy metals and can have many advantages, either alone or in combination with other supplements. There is no question that some biochars are an adequate solution-sorbent for heavy metals, but this is not an evidence of their effectiveness in handling heavy metals in the environment, as a wide range of confusing ecological, biological, and physical (ecosystem) synergies must also be considered.

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