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Quantifying the acceptance and adoption dynamics of biochar and co-biochar as a sustainable soil amendment

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Abstract

Biochar, a carbonized biomass, can be used as a soil amendment for improving soil fertility and productivity as well as ensuring agricultural sustainability. Biochar can be produced from different materials and at different conditions, so its quality varies greatly as a soil amendment. In this respect, the present study aimed to explore the effectiveness of 4 biochars as a soil ameliorator for securing soil health. The biochars were produced from 3 different biomasses *viz*., rice straw, sawdust and water hyacinth and their mixture (co-biochar at 1:1:1) at 400 °C. The biomasses and the biochars were characterized and the results revealed that conversion of biomasses into biochars caused a significant (p<0.05) increase in almost all of the biochar properties. Among the 4 biochars, water hyacinth biochar showed higher ash content, water holding capacity, surface area and total P, K, S, Ca and Zn. So, water hyacinth biochar could be a better choice as a soil amendment than the other three biochars. However, rice straw biochar showed higher cation exchange capacity (CEC), total N and Na and conversion efficiency of C, N, P, K, Na and Zn. Whereas, the co-biochar illustrated higher yield and showed the second highest in fixed C, CEC, total S, Ca and Zn and also in conversion efficiency of C, P, S, Na, K and Ca. Finally, it can be assumed to produce a co-biochar using rice straw at a higher ratio which might have a high potential for C storage and for supplying all of the essential plant nutrients.

Keywords

co-biochar; C sequestration; sustainability; nutrient; conversion efficiency

Introduction

Bangladesh is one of the most densely populated (more than 1300 people/sq.km) mainland countries in the world, having 165.2 million people (1). The government is working continuously to meet the future demanding food challenges. As a part of this, the adoption of modern variety, deep irrigation, synthetic fertilizers and pesticides was introduced in Bangladesh in 1960 which is known as the Green Revolution (2). Though the yield of cereal crops increased during the last few decades, the country is facing problems with land degradation, increasing soil salinity and water pollution due to the excess use of groundwater, chemical fertilizers and pesticides. Organic fertilizer application to soil might be effective in long-term soil conservation under such conditions as it maintains soil structure and biodiversity and increases

water and nutrient holding capacity (3). Rapid decomposition of traditional organic fertilizers like composts, manures and crop residues under humid tropical conditions leads to repeated application (4) and subsequently contributes to increasing global warming through carbon emission (5). Moreover, the country has been suffering frequently from natural disasters because of climatic change. As a result, the agricultural sustainability in Bangladesh is in a threatened state.

The problems faced by the people of Bangladesh are immense and require multiple solutions. Biochar is an emerging multi-purpose innovation that is rapidly attracting the attention of researchers (4). Biochar, a more resistant carbon-rich organic material obtained from the thermal decomposition of biomass, can be used as a soil amendment, a tool for improving soil fertility and productivity while also fighting the global challenge of climate change. Biochar is much more stable than uncharred organic matter (6). Biochar can store carbon in the ground in a stable way since pyrolysis traps the carbon in it which otherwise would be released through decomposition. Its presence in the soil can improve water-holding capacity, increase soil fertility, contain organic carbon (OC) and plant nutrients in significant amounts and raise agricultural productivity. Several studies from lots of pot and field trials have demonstrated that suitable biochar amendment is effective in enhancing soil's physical, chemical and biological properties, increasing the productivity of crops and reducing the bioavailability of inorganic and organic pollutants in soil. Amending the cropland with biochar might increase water holding capacity (WHC) and cation exchange capacity (CEC) and disease resistance of plants due to high surface area (SA) and high porosity. Biochar has been serving as an agent for both soil remediation (since it is a cost-effective carbon-based absorbent having high active functional groups) and carbon sequestration (7).

Biochar might be a better solution for Bangladesh regarding soil health and sustainable agriculture. Though over the past decade, biochar has been studied intensively throughout the world, limited studies regarding biochar have been undertaken in Bangladesh. Due to the ample availability of biomass, Bangladesh has the potential to produce biochar to solve these problems. Rice (*Oryza sativa* L.) straw constitutes the highest percentage (62%) of biomass originating from the agriculture sector. Besides, Bangladesh produces a total of 17 million tons of forest residues each year in the annual production of sawdust was 0.123 million tons (4). On the other hand, water hyacinth (*Eichhornia crassipes*), an aquatic weed, is one of the most pernicious invasive weeds that contain worthy nutrients for plant growth and are therefore a potential source of organic matter (8). These organic matters are valuable resources when properly managed and applied to soils, both as a fertilizer and as a soil amendment.

Biochar can be produced by the pyrolysis process in which organic materials are heated (>250 °C) in a limited or no oxygen environment (9). As biochar can be produced from diversified materials and at various conditions

(production temperature, heating rate, time, O_2 levels, feedstock etc.), its efficacy in improving soil properties also varies greatly. The heterogeneity in the qualities of biochar and the lack of standardization make it challenging to upgrade biochar technology, mass implementation and biochar adoption (10). More research is required in Bangladesh to produce and evaluate different biochar for exploring suitable biochar to use as soil amendments. Pyrolysis temperature is the most important condition that controls the nutrient composition and availability of biochar. Up to 50% of N, K and S are commonly lost when temperatures exceed 500 °C. To maintain high nutrient contents and availability, it is therefore preferable to keep the temperature low-for example, at or below 400 °C to 500 °C (6). It is suggested to characterize biochar before various applications since biochar may contain some compounds that could be harmful to plants despite having numerous benefits. Moreover, a single feedstock biochar can be poor in fertilizer value for its low-quality biomass. Such a problem can be solved by producing co-biochar through co-pyrolysis. When a pyrolysis process deals with more than one feedstock (blending 2 or more feedstocks) in the same operation is called co-pyrolysis. Co-pyrolysis process importantly increases the value of the biochar for widening its utilization, such as application in the field as an alternative organic conditioner (11).

Considering all the preceding information, the present study aimed to evaluate the potentiality of rice straw biochar, sawdust biochar, water hyacinth biochar and their co-biochar as a soil conditioner for sustainable agriculture.

Materials and Methods

Experimental site

The research (biochar production and characterization of the biomasses and the biochars) was carried out in the laboratories of Soil, Water and Environment Discipline, Khulna University (N 22° 89′/ E 89° 50′), Bangladesh.

Feedstock collection and biochar production

Three different biomasses (viz., rice straw, sawdust and water hyacinth) were selected for biochar production. Biomasses were selected based on their availability and keeping in mind the waste management concept. The materials were collected from the locality. Rice straw and water hyacinth were cut into 2-3 cm segments. The mate-rials were air dried to reduce excess moisture, dried in an oven at 80 °C for 48 h to a constant weight and then they were preserved for biochar production. The biochars were produced through a slow pyrolysis process using a muffle furnace under limited oxygen conditions (12). Biochars were produced at 400 °C to maintain high nutrient contents (6). From each of the three biomasses, one single biochar was produced and a co-biochar was produced by mixing the 3 materials at the same ratio by weight. The materials were placed in a rectangular stainless-steel box (19 cm × 9 cm × 3.8 cm) with a perforated lid and then placed in a muffle

furnace for thermal decomposition. The general information on biochar production is presented in Table 1.

Table 1. General information on biochar production.

Feedstock	Biomass code	Biochar code	Pyrolysis temperature (°C)	Residence time (min.)
Rice straw	RS	RSB	400	10
Sawdust	SD	SDB	400	15
Water hyacinth	WH	WHB	400	10
Rice straw: sawdust: water hyacinth at 1:1:1	RSW	RSWB	400	12

Biomasses and biochars sample preparation and characterization

The oven-dried biomasses were ground with an electric mortar and passed through 0.5 mm sieves for laboratory analysis. The biochar samples were homogenized, ground with mortar and pestle and then passed through 2 mm and 0.5 mm sieves for use in laboratory analysis (13). All the parameters analyzed were replicated 3 times.

Proximate analysis of biomasses and biochars

The proximate analysis estimates the % of ash, volatile matter (VM) and fixed carbon (C) content in biomasses and biochar samples. The procedure to estimate each of these quantities is based on ASTM methods as follows:

Ash content

The Ash content of the biomasses and biochars was determined by heating the dry (at 105 °C to constant weight) samples to 750 °C in an air atmosphere using the same muffle furnace for 6 h (14). The percent ash (% Ash) was determined using the following Eqn. 1.

$$\% \text{ Ash} = \frac{\text{Weight}_{\text{residue after 750 °C}}}{\text{Weight}_{\text{105 °C dried}}} \times 100$$

(Eqn. 1)

Volatile matter (VM)

The volatile matter of the biomasses and biochars was determined by heating the dry (at 105 °C to constant weight) samples to 950 °C for 10 min using the muffle furnace and then cooled in desiccators (14). The % volatile matter was determined using the following Eqn. 2.

$$\% \text{ Volatile matter} =$$

$$\frac{\text{Weight}_{\text{after 105 °C dried}} - \text{Weight}_{\text{950 °C devolatilised}}}{\text{Weight}_{\text{105 °C dried}}} \times 100$$

(Eqn. 2)

Fixed C

The fixed carbon of the biomasses and the biochar was calculated from the following Eqn. 3 (14):

$$\% \text{ Fixed carbon} =$$

$$\frac{\text{Weight}_{\text{105 °C dried}} - \text{Weight}_{\text{950 °C devolatilised}} - \text{Weight}_{\text{residue after 750 °C}}}{\text{Weight}_{\text{105 °C dried}}} \times 100$$

(Eqn. 3)

Physical properties of biochar

Water holding capacity

The water holding capacity (WHC) of the biochar was determined by suspending 100 g (W_{initial}) of dry sample in 1 L of water for 24 h, after which it was filtered and the wet weight of the sample was determined as W_{final} (15). To determine the water holding capacity by mass, the following equation was used:

$$\text{Water holding capacity (\%)} = \frac{W_{\text{final}} - W_{\text{initial}}}{W_{\text{initial}}} \times 100$$

(Eqn. 4)

Yield

Biochar yield was calculated using the following formula (16):

$$\text{Biochar yield (\%)} = \frac{\text{Weight of biochar}}{\text{Weight of biomass}} \times 100$$

(Eqn. 5)

Physico-chemical properties of biochar

Surface area of biochar

The surface area of the biochars was estimated according to Sears's method for silica-based materials as described in (17).

pH

The pH of the biochar was determined electrochemically with a pH meter using a modified dilution of 1:20 biochar: deionized H_2O (w:v) and equilibration at 90 min on the shaker (18).

Electrical conductivity (EC)

The EC of biochar was determined electrochemically with an EC meter using a modified dilution of 1:20 biochar: deionized H_2O (w: v) and equilibration at 90 min on the shaker (18).

Cation exchange capacity (CEC)

The CEC was determined by extracting the biochar with 1N KCl (pH 7.0) followed by replacing the potassium in the exchange complex with NH_4OAc. The displaced potassium was determined by a flame analyzer at 589 nm (19).

Chemical properties of biomasses and biochars

C content

C content of the biomasses and biochars was determined using the loss on ignition (LOI) method as described by burning the dry (at 105 °C to constant weight) samples in a muffle at 650 °C for 6 h in an open silica crucible (20).

Total nitrogen (N) of biomass and biochar

The total nitrogen of the samples was determined by Micro-Kjeldahl's method following H_2SO_4 acid digestion as suggested by (19).

Total P, S, Na, K, Ca, Mg and Zn

For the total nutrient analysis, the samples were subjected to wet digestion with HNO_3-$HClO_4$ (2:1) acid mixture to con-

vert the nutrients into water-soluble form (21). Then P in the digest was determined by the colorimetric method using absorption spectrophotometry and total SO_4-S in the digest was determined by the Turbidimetric method using absorption spectrophotometry. Na, K, Ca, Mg and Zn were determined using inductively coupled plasma (ICP)– optical emission spectroscopy (OES).

Statistical analysis

Data were analyzed statistically following the ANOVA technique using Minitab 19.0 software. Statistical analyses were done to establish whether there was a correlation between the properties of the biomasses and biochars through Pearson correlation. Significant variations and comparisons among data were analyzed through one-way ANOVA and paired *t*-tests. Significant differences among the biochar properties were calculated by using Tukey's tests at P<0.05. Other calculations done using Microsoft Excel 2010.

Results and Discussion

Proximate analysis

The results of the proximate analysis carried out on the biomasses (RS, SD, WH and RSW) and biochars (RSB, SDB, WHB and RSWB) are presented in Table 2. Statistical analysis of the results revealed that biomasses varied significantly (at p<0.05) in ash content, VM and fixed C (Table 2). In the case of ash content, WH produced the highest amount (17.27±0.48%) of ash which was significantly (p<0.001) higher than that of the others (Table 2). The lowest ash content was produced by SD (8.67±0.50%). RS had the highest VM content (77.21±0.91%) which was statistically similar to that of SD and RSW but significantly (p<0.05) higher than that of WH. The lowest amount of VM was produced by WH (74.70±1.04 %).

Table 2. Proximate analysis of biomasses and biochars.

Sample		Properties (Wt.%, dry basis)		
		Ash	**VM**	**Fixed C**
Biomass	RS	10.59±0.26[c]	77.21±0.91[a]	12.20±0.66[b]
	SD	8.67±0.50[d]	76.96±1.03[ab]	14.37±0.55[a]
	WH	17.27±0.48[a]	74.70±1.04[b]	8.03±0.58[c]
	RSW	12.16±0.14[b]	76.30±0.16[ab]	11.54±0.09[b]
Biochar	RSB	28.63±0.49[b]	25.16±0.26[b]	46.20±0.56[c]
	SDB	7.53±0.42[d]	27.81±0.62[a]	64.66±0.54[a]
	WHB	37.47±0.95[a]	20.05±0.54[c]	42.48±0.41[d]
	RSWB	24.54±0.51[c]	24.34±0.20[b]	51.11±0.42[b]

Values are given as mean ± standard deviation (n = 3), Mean data in a column followed by different letter(s) are statistically significant according to Tukey's tests at P= 0.05, Here, **RS**=rice straw, **SD**=sawdust, **WH**=water hyacinth, **RSW**= Rice straw: sawdust: water hyacinth at 1:1:1, **RSB**= rice straw biochar, **SDB**=sawdust biochar, **WHB**=water hyacinth biochar, **RSWB**=co-biochar, **VM**=volatile matter.

SD showed the highest amount (14.37±0.55%) of fixed C and it was significantly (p<0.001) higher than that of the others. WH had the lowest fixed C (8.03±0.58%) content (Table 2). The results of the present study were in line

with several studies. Previous studies reported 13.91% ash, 76.32% VM and 9.08% fixed C for rice straw (22). For sawdust, it was indicated 11.95% ash, 75.16% VM and 6.87% fixed C in the previous studies (23) whereas, 14.56% ash, 71.27% VM and 14.56% fixed C for water hyacinth (24). All of the investigators represented their results in wt.%, dry basis. The previous studies demonstrated a similar trend of variation of ash, VM and fixed C contents of the biomasses in the current studies.

The volatile matter was mainly derived from cellulose and hemicellulose, where fixed C was obtained solely from the lignin component of biomass. The ash content is the residue after the combustion of the volatile matter content of the biomass material (24). Table 3 presents the biochemical composition of the biomass materials. All the information from the previous literature strongly supported the biomasses proximate analysis results of the present study.

Table 3. Bio-chemical composition of the biomass materials.

Biomasses	Lignin (wt.%)	Cellulose (wt.%)	Hemicellulose (wt.%)	References
RS	14.5	34	36.06	(25)
SD	33.2	40.1	26.7	(23)
WH	6.10	26.5	27.90	(24)

Like the source materials the produced biochars were also significantly (p<0.001) varied in ash content, VM and fixed C (Table 2). The highest amount (37.47±0.95%) of ash was produced by WHB which was significantly (p<0.001) higher than the others and the lowest ash content was produced by SDB (7.53±0.42%). SDB had the highest VM content (27.81±0.62%) which was significantly (p<0.001) higher than that of the others. The lowest amount of VM was produced by WHB (20.05±0.54%). Previous observations confirmed the results of the present study (24). They stated that woody biomass-derived biochars show a larger weight loss as they contain higher volatile materials than non-woody biochars. Among the 4 biochars, SDB contained the highest amount (64.66±0.54%) of fixed C and it was significantly (p<0.001) higher than that of the others and WHB contained the lowest amount (42.48±0.41%) of fixed C (Table 2). It was observed that 25.71% ash, 21.14% VM and 53.15% fixed C for RSB were produced at 400 °C (22). The results of the proximate analysis of RSB were consistent with the previous study. In the present study, the results of proximate analysis of SDB differ greatly from previous investigations where, SDB was also produced at 400 °C but observed lower ash (1.94%) content, much higher VM (72.00%) and lower fixed C (31.40%) (26). For WHB, scientists illustrated lower ash (14.45%) but similar VM (25.74%) and fixed C (49.69%) % where the biochar was also produced at 400 °C (27). In the previous studies, co-biochar was produced with pine cones and vegetable wastes at a 1:1 blend ratio, pyrolyzed at 500 °C and observed slightly lower ash (18.1%) and VM (10.3%) but higher fixed C (70.5%) content in compare to this study (28).

Irrespective of the source materials, the ash, VM and

fixed C content of the biomasses were strongly positively and significantly correlated with ash content (r =0.853; p<0.001), VM content (r = 0.754; p<0.01) and fixed C (r =0.838; p<0.001) content of the produced biochars respectively (Table 4). Therefore, the ash, VM and fixed C content of the biochars were highly dependent on that of the biomasses.

The thermal decomposition of the biomasses signi-

Table 4. Pearson correlation (r) matrix of biomass ash, biomass VM, biomass fixed C, biochar ash, biochar VM and biochar fixed C at p=0.05.

	Biomass ash	Biomass VM	Biomass fixed C	Biochar ash	Biochar VM
Biomass VM	-0.823				
Biomass fixed C	-0.955	0.618			
Biochar ash	0.853***	-0.544	-0.898		
Biochar VM	-0.984	0.754**	0.968	-0.911	
Biochar fixed C	-0.776	0.452	0.838**	-0.990	0.845

***p<0.001; **p<0.01, Here, **VM**=volatile matter.

ficantly increased the ash (t = -4.93, p < 0.001) and fixed C (t = -19.93, p < 0.001) content and significantly decreased the VM (t = 83.71, p < 0.001) content of the produced biochars from the ash, fixed C and VM content of the biomasses respectively (Table 5) where the biomass materials were not differentiated.

readily mineralizable fraction of biochars. Fixed C content represents the C sequestration potential of biochar (14). Therefore, the lower the VM and the higher the fixed C content the higher the C fixation or removal from the environment.

Physical and physico-chemical properties of biochars

The results of the physical and physico-chemical properties of the produced biochars (RSB, SDB, WHB and RSWB) are presented in Table 6. According to the results, the biochars produced from different biomasses varied greatly in their WHC, yield, surface area, pH, EC and CEC values. Excluding CEC all other parameters varied significantly (p<0.001) among the biochars (Table 6). Results revealed high WHC of the biochars with considerable differences (Table 6). The WHC of the biochars ranged from 3.84±0.08 mL g^{-1} (384%) (for SDB) to 4.77±0.05 ml g^{-1} (477%) (for WHB) (Table 6). WHB showed significantly higher WHC than others but it was statistically similar for RSB and co-biochar. So, application of the biochar to soil might be very effective for reducing irrigation requirements since crop production depends enormously on fertilizers and irrigation. Agricultural practices in an unsustainable way have led in large areas to unproductive sandy soils with lower WHC. The biochars could be a new hope and competent amendment for light-textured soil because of their high WHC. From previous investigations, slightly higher WHC values were reported for RSB (479%) and WHB (495%) which were

Table 5. Paired t-test and CI: Biomass, Biochar.

Sample		N	Mean	StDev	95% CI for mean difference	t-Value	P-Value
Ash	Biomass	12	12.16b	3.35	-17.90	-4.93	0.000
	Biochar	12	24.54a	11.37	-6.86		
VM	Biomass	12	76.292a	1.261	50.585	83.71	0.000
	Biochar	12	24.342b	2.935	53.316		
Fixed C	Biomass	12	11.53b	2.42	-43.95	-19.93	0.000
	Biochar	12	51.11a	8.78	-35.21		

Mean data in a column followed by a different letter(s) are statistically significant according to Tukey's tests at P = 0.05, Here, **VM**=volatile matter, **StDev**= standard deviation, **CI**= confidence interval.

Table 6. Physical and physico-chemical properties of the produced biochars.

Properties	Biochar			
	RSB	SDB	WHB	RSWB
WHC (ml g^{-1})	4.54±0.05b	3.84±0.08c	4.77±0.05a	4.42±0.08b
Yield (%)	40.02±0.86b	43.51±1.02a	37.80±0.50c	44.53±0.74a
Surface area (m^2g^{-1})	164.87±1.85c	190.47±1.86b	205.40±3.2a	188.24±1.02b
pH	8.28±0.06a	7.89±0.02c	8.06±0.02b	7.27±0.06d
EC (dSm^{-1})	6.77±0.15b	0.43± 0.06c	13.03±0.32a	6.63±0.04b
CEC	37.86±6.43a	28.97± 5.44a	35.56±0.00a	36.88±2.01a

Values are given as mean ± standard deviation (n = 3), Mean data in a row followed by a different letter(s) are statistically significant according to Tukey's tests at P= 0.05, Here, RSB= rice straw biochar, SDB=sawdust biochar, WHB=water hyacinth biochar, RSWB=co-biochar.

Biochar contains higher ash content than biomass which is rich in plant nutrients (14). Biochars are commonly regarded as OC-rich materials (6). The conversion of biomasses into biochars caused a decrease in VM content. The finding of the present study is an indication of the increasing stability of the biochars. On the other hand, VM gives relative measures of the labile OC fraction as well as the

produced at 380±20 °C (29). Similar findings were reported for WHC (395%) of SDB also pyrolyzed at 400 °C (26). In the case of biochar yield, the results revealed that the co-biochar had the highest yield (44.53±0.74%). This enhanced yield of the co-biochar over its component biochar is consistent with the previous findings (30) due to positive synergistic effects. The lowest yield was observed for WHB

(37.80±0.50%) but the yield of SDB and the co-biochar were statistically the same. Similar findings were observed for RSB (31) and for WHB (27) which were also produced at 400 °C. There was also a findings produced sawdust biochar at 400 °C also but observed a higher yield (55%) than the present study. The yield of co-biochar was in close agreement with some previous studies produced co-biochar with sewage sludge and sawdust at the ratio of 1:1 (pyrolyzed at 400 °C) and observed 44.51% yield (11). A study produced co-biochar with wheat straw, rice husk, pig manure and oyster shells at the ratio of 3:3:3:1 (pyrolyzed at 450 °C) and found 42.3% yield of the co-biochar (7). The biochar surface area ranged from 164.87±1.85% (for RSB) to 205.40±3.2% (for WHB). The surface area of WHB was significantly (p<0.001) higher than that of the others. Biochars with greater surface area provide sites to fix more nutrients and heavy metals and adsorption of ions and water. When biochars are incorporated in soil the high surface area is likely to increase soil aeration, water holding capacity and nutrient retention (29). Several studies reported much lower surface area (25.46 m^2g^{-1} for RSB 83.90 m^2g^{-1} for SDB and 4.7 m^2g^{-1} for WHB) than that of the present study (26, 29, 31). The surface area of the co-biochar of this study was also found to be higher than that (2.78 m^2g^{-1}) investigated (11).

The pH of the biochars ranged from 7.27 (RSWB) to 8.28 (RSB), making it neutral to moderately alkaline. RSB had significantly (p<0.001) higher pH than that of the other biochars and the co-biochar had the lowest. Pyrolyzing temperature increases the pH value of biochars probably as a consequence of the relative concentration of non-pyrolyzed inorganic elements that are already present in the original feedstocks. Biochars produced from woody feedstocks with low ash content generally have lower pH than biochars produced from grass, crop residues or manures with higher ash content (14). The results of the present study were found to strongly agree with this statement. This high pH of biochar could be helpful to reduce Al toxicity and to increase P availability by amending the acid soils with suitable biochar. Electrical conductivity (EC) was very high for RSB, WHB, and RSWB whereas SDB had relatively lower EC (Table 6). The EC ranged between 0.43 and 13.03 dS m^{-1} equivalent to 0.03% and 0.83% salt respectively, which indicated the presence of low to very high soluble salt content in the biochars. WHB had significantly (p<0.001) higher and SDB had significantly (p<0.001) lower EC than that of the other biochars. However, the EC of RSB and the co-biochar were statistically the same. The CEC varied insignificantly (p>0.05) among the biochars (Table 6). It ranged from 28.97 Cmol$_c$ Kg^{-1} (for SDB) to 37.86 Cmol$_c$ Kg^{-1} (for RSB). The difference in CEC values might be due to the varying K content in the biochars (Table 7). K, Ca, Mg, Na and P in the feedstock promote the formation of O-containing groups on the biochar surface during pyrolysis and result in higher CEC. For improving soil fertility of low-fertility sandy soils, the biochars can be an interesting soil amendment. Biochars with high CEC can also be used for remediating soil or water that is contaminated with heavy metals (32).

Table 7. Total C in biomasses and biochars.

Properties (%)	Results			
Biomass C	RS	SD	WH	RSW
	42.28±0.64b	55.43±0.62a	32.74±0.57c	41.41±1.20b
Biochar C	RSB	SDB	WHB	RSWB
	75.07±0.31b	88.47±0.42a	55.70±0.46d	73.10±0.36c

Values are given as mean ± standard deviation (n = 3), Mean data in a row followed by different letter(s) are statistically significant according to Tukey's tests at P= 0.05, Here, **RS**=rice straw, **SD**=sawdust, **WH**=water hyacinth, **RSW**= Rice straw: sawdust: water hyacinth at 1:1:1, **RSB**= rice straw biochar, **SDB**=sawdust biochar, **WHB**=water hyacinth biochar, **RSWB**=co-biochar.

Literature showed varying observations from the biochar physico-chemical properties of the present study. It was observed similar pH (8.1), but a much lower EC (0.85 dS m^{-1}) and much higher CEC (65.3 Cmol$_c$ Kg^{-1}) for RSB (33, 34). Lower pH (6.35) but higher EC (2.44 dS m^{-1}) and similar CEC (27.5 Cmol$_c$ Kg^{-1}) were reported for SDB (26). For WHB, similar results were published for pH but lower values for EC (7.38 dS m^{-1}) and CEC (27.35 Cmol$_c$ Kg^{-1}) (29). It was explored much higher pH (9.55) but much lower EC (0.045 dS m^{-1}) for co-biochars (1, 28). For co-biochar produced from cotton stalks-sewage sludge (at 9:1 blending ratio) pyrolyzing at 650 °C, lower CEC (22.5 Cmol$_c$ Kg^{-1}) was reported (30). The observed variation might be due to their difference in source materials and/or production conditions.

Chemical properties of biomass and biochar

The results of the chemical analysis of the biomasses and the produced biochars were summarized in Tables 7 and 8. All of the biomasses were significantly (at p=0.05) varied in C and other nutrient contents. The C content of the biomasses ranged from 80.53±0.61% (for WH) to 90.23±0.32% (for SD). SD had significantly (p<0.001) higher C content than that of the others but that of RS and RSW were statistically similar. The total N content in biomass ranged from 0.50±0.00% (for SD) to 0.78±0.14% (for RS and WH). SD and the RSW had statistically similar N content. RS and WH had significantly (p<0.05) higher N than others.

SD had the lowest P (0.67±0.07 g Kg^{-1}), K (0.46±0.1g Kg^{-1}), S (0.53±0.07g Kg^{-1}) and Na (0.16± 0.02 g Kg^{-1}) content and RS had the lowest Ca (7.33±0.58 g Kg^{-1}), Mg (5.00±0.69 g Kg^{-1}) and Zn (6.83±0.81 g Kg^{-1}) than that of the others. Among the biomasses analyzed in the study, WH had the highest P (5.48±0.28 g Kg^{-1}), K (1.46±0.26 g Kg^{-1}), S (4.63±0.02 g Kg^{-1}), Na (1.1±0.2 g Kg^{-1}), Ca (10.33±1.16 g Kg^{-1}) and Zn (42.01±0.80 g Kg^{-1}). The P, K, S, Na and Zn contents of WH were significantly (p<0.001) higher than those of the others. In the case of Mg content, SD had the highest value (8.00±0.35 g Kg^{-1}) than that of the others which was significant (p<0.01) also (Table 8). For RS, scientists reported considerably lower C (38.01%), N (0.58%), P (1 g Kg^{-1}), S (0.8 g Kg^{-1}), Ca (1.7 g Kg^{-1}) and Mg (1.1 g Kg^{-1}) but higher values of Na (1.3g Kg^{-1}), K (2 g Kg^{-1}) and much higher Zn (30 g Kg^{-1}) than that of the present study (25, 31, 35, 36). In previous studies, investigators illustrated much lower C (41.38%) but higher N (0.66%), P (1.2 g Kg^{-1}), S (2.8 g Kg^{-1}), K (3.36 g Kg^{-1}), Na (1.44 g Kg^{-1}) and lower Ca (4.67 g Kg^{-1}), Mg (1.75 g Kg^{-1}) and surprisingly very much higher Zn (2590 mg

Kg^{-1}) for sawdust in their study (37-39). Previous studies showed very low C (34.67%) but very high values of N (5.6%) P (12.40 g Kg^{-1}), S (33.90 g Kg^{-1}), K (4.20 g Kg^{-1}), Na (2.20 g Kg^{-1}) and Zn (50.8 mg Kg^{-1}) but lower values of Ca (6.60 g Kg^{-1}) and Mg (1.70 g Kg^{-1}) for WH (29, 40, 41) than that of the present study.

The results of the chemical analysis of the produced biochar revealed that the biochar significantly (at p<0.05)

cantly the highest content of N and Na. The lowest content of N, P, K, S, Na and Zn and the lowest content of Ca and Mg were observed for SDB and RSB respectively (Tables 7 and 8).

Previous literature showed very surprising results for the biochar's chemical properties. They reported variable results of the parameters for a single biochar in comparison to the current study. Previous studies reported

Table 8. Total nutrient (N, P, K, S, Na, Ca, Mg and Zn) status of the biomasses and the produced biochars

Nutrients	Biomasses			
	RS	**SD**	**WH**	**RSW**
N (%)	0.78±0.14a	0.50±0.00b	0.78±0.14a	0.67±0.03b
P (g Kg^{-1})	1.05±0.08c	0.67±0.07c	5.48±0.28a	2.35±0.07b
K (g Kg^{-1})	0.99±0.01b	0.46±0.1c	1.46±0.26a	0.97±0.08b
S (g Kg^{-1})	1.47±0.12c	0.53±0.07d	4.63±0.02a	2.21±0.02b
Na (g Kg^{-1})	0.47±0.02b	0.16± 0.02c	1.1±0.2a	0.58±0.03b
Ca (g Kg^{-1})	7.33±0.58b	8.33± 0.58ab	10.33±1.16a	8.67±0.67ab
Mg (g Kg^{-1})	5.00±0.69b	8.00±0.35a	6.4±0.92b	6.47±0.23ab
Zn (mg Kg^{-1})	6.83±0.81d	12.14±1.32c	42.01±0.80a	20.33±0.44b
	Biochars			
	RSB	**SDB**	**WHB**	**RSWB**
N (%)	1.84±0.20a	0.18±0.04c	1.38±0.20b	1.13±0.13b
P (g Kg^{-1})	9.89± 0.50a	1.62 ±0.26c	10.67±0.51a	7.39±0.12b
K (g Kg^{-1})	4.51±0.18b	1.03±0.18d	5.21±0.15a	3.58±0.05c
S (g Kg^{-1})	2.07±0.18c	1.76±0.06c	6.62±0.29a	3.48±0.14b
Na (g Kg^{-1})	2.62±0.23a	0.39±0.02c	1.97±0.02b	1.66±0.11b
Ca (g Kg^{-1})	19.17±3.82c	21.67±1.44bc	31.67±1.44a	25.33±0.76b
Mg (g Kg^{-1})	14.5±0.87c	28.5±1.50a	25.50±2.60ab	22.83±0.29b
Zn (mg Kg^{-1})	39.35±2.32c	21.81±0.13d	184.45±0.93a	81.87±0.42b

Values are given as mean ± standard deviation (n = 3), Mean data in a row followed by different letter(s) are statistically significant according to Tukey's tests at P= 0.05, Here, **RS**=rice straw, **SD**=sawdust, **WH**=water hyacinth, **RSW**= Rice straw: sawdust: water hyacinth at 1:1:1, **RSB**= rice straw biochar, **SDB**=sawdust biochar, **WHB**=water hyacinth biochar, **RSWB**=co-biochar

varied in their C and other total nutrient content. Sawdust biochar had significantly (p<0.001) the highest C content (88.47±0.42%) and water hyacinth biochar had the lowest C (55.70±0.46%) content than that of the others. Tables 7 and 8 demonstrated that the C and other nutrient contents were increased in the biochars from their respective biomasses (excluding the N content of SDB). The N content in SDB was decreased due to pyrolysis from its biomass. Similar findings were narrated in the previous study where they claimed to decrease total N content in farmyard manure biochar, water hyacinth biochar, corn cob biochar and rice straw biochar from their biomasses. Previous studies also confirmed this finding that the N loss was increased with increasing temperature and the remaining N was transformed into the form of heterocyclic-N. High pyrolysis temperature resulted decrease in available N due to the loss of total N as well as N heterocyclization which also assured the fact that total nutrient content might not always represent the real availability of nutrients to plants (32). Table 8 demonstrated that WHB had significantly the highest content of P, K, S, Ca and Zn, and RSB had signifi-

similar C content (72.38%) but higher TN (3.16%), low P (5.60 g Kg^{-1}) but very high K (36.40 g Kg^{-1}) and S (7.70 g Kg^{-1}) for RSB (22, 29). For RSB, another study reported very lower Ca (0.019 g Kg^{-1}), Mg (0.014 g Kg^{-1}), and Na (0.013 g Kg^{-1}) but very higher (58.0 mg Kg^{-1}) where RSB was produced at >400° C (42). On the other hand, very low C (52.99%) but very high N (2.01%), similar results of P (1.48 g Kg^{-1}), K (0.783 g Kg^{-1}), Na (0.313 g Kg^{-1}), lower results of S (0.53 g Kg^{-1}), Ca (1.51 g Kg^{-1}), Mg (1.23 g Kg^{-1}) and higher results of Zn (62.32 g Kg^{-1}) were reported for SDB (43, 44). For WHB, low C (37.22%), high N (1.04%), and very high P (19.90 g Kg^{-1}), K (74.90 g Kg^{-1}), and S (19.20 g Kg^{-1}) were reported (29). much lower Ca (9.5 g Kg^{-1}), Mg (3.8 g Kg^{-1}), Na (0.7 g Kg^{-1}), and very high Zn (645 mg Kg^{-1}) were demonstrated for WHB produced at 300 °C (8). Previous studies indicated very lower C (31.22%) and Mg (7.74 g Kg^{-1}) but slightly to very high N (2.10%), P (17.62 g Kg^{-1}), K (15.13 g Kg^{-1}), S (5.30 g Kg^{-1}), Ca (90.78 g Kg^{-1}) and Zn (194.24 g Kg^{-1}) for co-biochar (7, 11).

Tables 8 and 9 demonstrated that the C content of feedstock determined significantly (at p<0.05) the restored

carbon in the produced biochars. The C and other total nutrients (N, P, S, Na, K, Ca, Mg and Zn) of biomasses were strongly positively and also significantly (except Na) correlated with the C (r =0.969; p<0.001), N (r = 0.759; p<0.01), P (r =0.620; p<0.05), S (r =0.981; p<0.001), Na (r =0.514; p>0.05), K (r =0.886; p<0.001), Ca (r =0.907; p<0.001), Mg (r =0.791; p<0.01), and Zn (r =0.970; p<0.001) content of the produced biochars (Table 9 and 10) irrespective of the source materials. Therefore, the biomass with higher levels of nutrients might produce biochar with higher nutrients also.

Thermal decomposition alters the C and other total

conversion efficiency of the biochars. The biochars significantly (at p<0.05) differed in conversion efficiency of almost all of the parameters (excluding Ca and Mg). C conversion efficiency ranged from 159.62% to 177.58% depending on the materials used as feedstock (Table 12). C conversion efficiency was the lowest for SDB though it had the highest amount of C (88.47%) among the others and RSB exhibited the highest (177.58%) efficiency at 400 °C followed by co-biochar and WHB but the efficiencies of the latter 3 were statistically similar. RSB illustrated the second-highest C content among the biochars (Table 7).

N conversion efficiency varied from a lower 35.26% to a higher 237%. RSB showed significantly (p<0.001) the high-

Table 9. Pearson correlation (r) matrix of biomass C, biomass N, biomass P, biomass S, biochar C, biochar N, biochar P and biochar S at p<0.05.

	Biomass C	Biomass N	Biomass P	Biomass S	Biochar C	Biochar N	Biochar P
Biomass N	-0.720						
Biomass P	-0.843	0.472					
Biomass S	-0.913	0.543	0.986				
Biochar C	0.969***	-0.659	-0.939	-0.980			
Biochar N	-0.725	0.759**	0.310	0.443	-0.606		
Biochar P	-0.924	0.799	0.620*	0.730	-0.849	0.928	
Biochar S	-0.841	0.429	0.990	0.981***	-0.930	0.280	0.604

***p<0.001; **p<0.01; *p<0.05.

Table 10. Pearson correlation (r) matrix of biomass K, biomass Na, biomass Ca, biomass Mg, biomass Zn, biochar K, biochar Na, biochar Ca biochar Mg and biochar Zn at p<0.05

	Biomass Na	Biomass K	Biomass Ca	Biomass Mg	Biomass Zn	Biochar Na	Biochar K	Biochar Ca	Biochar Mg
Biomass K	0.831								
Biomass Ca	0.734	0.394							
Biomass Mg	-0.297	-0.521	0.209						
Biomass Zn	0.862	0.720	0.854	0.096					
Biochar Na	0.514^{NS}	0.671	-0.061	-0.900	0.098				
Biochar K	0.827	0.886***	0.307	-0.709	0.510	0.890			
Biochar Ca	0.803	0.609	0.907***	0.091	0.932	0.080	0.441		
Biochar Mg	0.030	-0.264	0.571	0.791**	0.422	-0.823	-0.514	0.458	
Biochar Zn	0.944	0.849	0.786	-0.122	0.970***	0.327	0.701	0.894	0.210

***p<0.001; **p<0.01; *p<0.05; *NS*- not significant.

nutrient content in the resulting biochars from their biomasses (Tables 7 and 8). The statistical analysis (paired *t*-test) revealed that the thermal decomposition of the biomasses significantly increased the C (t = -23.41; p<0.001), N (t = -2.82; p<0.05), P (t = -5.91; p<0.001), S (t = -7.98; p<0.001), Na (t = -5.09; p<0.001), K (t = -6.81; p<0.001), Ca (t = -13.30; p<0.001), Mg (t = -12.07; p<0.001), and Zn (t = -4.07; p<0.01) content of the produced biochars from that of the biomasses (Table 11) where the biomasses were considered as single material.

Due to the increment of C and other nutrients in the resulting biochar, nutrient availability to plants could be affected. The increase in carbon and other nutrient status during pyrolysis means, loss of volatile components (H and O mainly) of the source material and relatively small losses of alkali nutrients by volatilization. The influence of biomass on carbon and nutrient recovery in biochar varied greatly (29). Table 12 summarizes the C and other nutrient

est (237%) N conversion efficiency than others having 1.84% N stored in it and SDB exhibited the lowest (35.26%) efficiency. WHB and RSWB were statistically similar in N conversion efficiency (Table 12). In the present study, the produced biochars showed a huge difference in P conversion efficiency and were the highest (195.31% to 942%) among all nutrients. WHB exhibited the lowest efficiency though WHB illustrated the highest (10.67 g Kg^{-1}) P concentration among the others. The highest efficiency was demonstrated by RSB having (9.89 g Kg^{-1}) P concentration. Total P content increased significantly (P = 0.05) with increasing pyrolysis temperature, not like total N where the available form increased when it was produced at low-temperature (≤400 °C) (45). Therefore, biochars produced at low temperatures like those in the present study also may be a good amendment to fortify P content in P-deficient soils.

S conversion efficiency of the produced biochars varied

Table 11. Paired *t*-test and CI: Biomass, Biochar.

	Sample	N	Mean	StDev	95% CI for mean difference	*t*-Value	P-Value
C	Biomass	12	42.96b	8.49	-32.96	-23.41	0.000
	Biochar	12	73.09a	12.17	-27.30		
N	Biomass	12	0.68b	0.15	-0.79	-2.82	0.017
	Biochar	12	1.13a	0.65	-0.10		
P	Biomass	12	2.39b	1.98	-6.87	-5.91	0.000
	Biochar	12	7.39a	3.72	-3.14		
S	Biomass	12	2.21b	1.58	-1.63	-7.98	0.000
	Biochar	12	3.48a	2.02	-0.92		
Na	Biomass	12	0.58b	0.36	-1.55	-5.09	0.000
	Biochar	12	1.66a	0.85	-0.61		
K	Biomass	12	0.97b	0.39	-3.45	-6.81	0.000
	Biochar	12	3.58a	1.66	-1.77		
Ca	Biomass	12	8.67b	1.30	-18.41	-13.30	0.000
	Biochar	12	24.46a	5.26	-13.18		
Mg	Biomass	12	6.47b	1.22	-19.35	-12.07	0.000
	Biochar	12	22.83a	5.61	-13.38		
Zn	Biomass	12	20.3b	14.0	-94.9	-4.07	0.002
	Biochar	12	81.9a	65.9	-28.2		

Mean data in a column followed by a different letter(s) are statistically significant according to Tukey's tests at P = 0.05, StDev= standard deviation, CI= confidence interval.

Table 12. C, N, P, S, Na, K, Ca, Mg and Zn conversion efficiency of the biochars.

Parameters	Conversion efficiency (%)			
	RSB	SDB	WHB	RSWB
C	177.58a	159.62b	170.19ab	176.72a
N	237.00a	35.26c	176.30b	166.79b
P	942.00a	242.9b	195.31b	314.46b
S	140.40b	334.7a	143.17b	157.61b
Na	556.90a	245.3bc	182.90c	285.54b
K	453.80a	228.00b	363.70a	371.30a
Ca	260.40a	260.40a	308.10a	292.82a
Mg	292.30a	356.23a	405.30a	353.13a
Zn	578.90a	181.20c	439.14b	402.92b

Mean data in a row followed by different letter(s) are statistically significant according to Tukey's tests at P= 0.05, Here, **RSB**= rice straw biochar, **SDB**=sawdust biochar, **WHB**=water hyacinth biochar, **RSWB**=co-biochar.

from 140.40% to 334.70%. Surprisingly, SDB showed significantly (p<0.001) the highest S conversion efficiency despite having the lowest S concentration (1.76 g Kg^{-1}) and RSB had the lowest efficiency. RSB exhibited significantly (p<0.001) the highest Na (556.9%; p<0.001) and K (453.8%; p<0.01) conversion efficiency whereas the lowest efficiency of Na was attributed to WHB (182.9%) and K was showed by SDB (228%) (Table 12). Literature reported similar findings like total P for total K but opposite for available K and they demonstrated a significant (P = 0.05) increase in water-soluble K content with increasing pyrolysis temperature. They also observed no loss of K during pyrolysis where, in another study, there was illustrated a 48% loss of total K during rice straw biochar production at temperatures between 473 and 673 °C (45).

Table 12 also demonstrated that the biochars insignificantly (p>0.05) varied in Ca and Mg conversion efficiency which ranged from 260.40% to 308.10% and 292.30% to 405.30% respectively. The highest Ca and Mg conversion efficiency was illustrated by WHB and the lowest value was exhibited by RSB, SDB and RSB respectively. For Zn conversion efficiency, the biochars varied significantly (p<0.001) among them and ranged from 181.2% to 578.90%. RSB had the highest Zn conversion efficiency having a lower (39.35 g Kg^{-1}) concentration followed by WHB and RSWB and SDB showed the lowest efficiency (181.20%).

The results of the present study revealed that due to the conversion of biomasses into biochars, the ash and fixed C were increased and VM was decreased which was the indication of higher nutrients and stability of the biochars. The results also revealed that beneficial physico-chemical properties (e.g., WHC, higher surface area, neutral to alkaline pH, higher CEC) were developed in the biochars. Enhanced nutrient retention may be attributed to improved soil physicochemical properties, such as the increase of porosity and WHC and the decrease of soil bulk density (46) since, biochars have higher surface area and porosity, low bulk density, higher CEC, neutral to high pH and higher C content (47). Besides, important total nutrient content was also intensified in the produced biochars depending on their feedstock composition. Among the 4 biochars, WHB showed significantly (at p=0.05) higher ash (higher fertilizer effect), WHC, surface area and total nutrients (P, K, S, Ca and Zn). Therefore, WHB could be a better choice as a soil amendment than other biochars. Amending soil with biochar improved fertilizer use efficiency and soil fertility by increasing nutrient availability and enhancing nutrient retention (i.e., reducing nutrient loss by leaching and emission) and release respectively (48). However, rice straw biochar illustrated higher CEC, significantly (at p=0.05) higher total N and Na and higher conversion efficiency of C, N, P, K, Na and Zn. Moreover, it showed the second highest in ash content, WHC, C, total P and K. Whereas, the co-biochar showed significantly (at p=0.05) higher yield and second highest in fixed C, CEC, total S, Ca and Zn and also second highest in conversion efficiency of C, P, S, Na, K and Ca. High biochar C content is greatly important since one of the main aims of biochar application is to sequester carbon in soil to mitigate climate change. By the year 2100, 9.5 billion tons of carbon can be potentially stored in the soils with biochar application (49) which may help not only in solving the problems with climate change but also in enhancing soil sustainability (6). Therefore, the application of biochars instead of their biomasses could be ideally preferable. From the results of this study, it can be assumed that a single co-biochar may be produced by using RS at a higher ratio which most possibly will contain higher fixed and total C as well as all of the essential plant nutrients.

Conclusion

Pyrolysis of biomasses caused significant changes in pro-

duced biochar properties. WHB exhibited higher ash content, WHC, surface area and total nutrients (P, K, S, Ca and Zn) suggesting good potentiality as a soil amendment than SDB, RSB and RSWB. However, RSB showed higher CEC, total N and Na and higher nutrient conversion efficiency whereas, RSWB showed higher yield and second highest in fixed C, CEC, total S, Ca and Zn and also in nutrient conversion efficiency. Finally, it is assumed to produce a co-biochar using RS at a higher ratio containing higher C and all of the essential plant nutrients.

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Authors contributions

MK, MH and JCJ were directly involved in the research planning and work design. MK performed the experiments under the guidance of MH and JCJ. MK collected the data and drafted the manuscript. MK and JCJ analysed the research data. All authors read and approved the final manuscript.

Compliance with ethical standards

Conflict of interest: Authors do not have any conflict of interests to declare.

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