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Chemical and Textural Properties of Melon Seed Shell-Derived Biochar Relevant to their Application in the Remediation of Contaminated Soil

Ogede, L.O., *Ejimadu, C.M. and Okieimen, F.E.

Centre for Biomaterials Research, Department of Chemistry, University of Benin, Benin City, Nigeria.
*ejimaduchima@gmail.com

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ABSTRACT

In this study, biochar samples obtained by pyrolysis of melon seed shells at different temperatures (300 – 450 ^oC) were characterized for their potential as amendment materials in the remediation of contaminated soil. It was found that the marked decrease in the yield of the biochar (56.60 – 29.70%) with increase in pyrolysis temperature was associated with an increase of about 2.0 pH units in the pH of the biochar samples. Surface morphology and Brunauer Emmett Teller (BET) particle analysis of the samples show that all the biochar samples are microporous. The BET surface are MSSB300 (288.42 $m^2.g^{-1}$), MSSB350 (355.36 $m^2.g^{-1}$), MSSB400 (472.28 $m^2.g^{-1}$), and MSSB450 (633.91$m^2.g^{-1}$) and the pore volume MSSB300 (0.18 $cm^3.g^{-1}$), MSSB350 (0.23 $cm^3.g^{-1}$), MSSB400 (0.29 $cm^3.g^{-1}$), and MSSB450 (0.36 $cm^3.g^{-1}$) ($cm^3.g^{-1}$) increasing with an increase in pyrolysis temperature. The elemental composition of the biochar samples gave relatively low levels of nutrient elements, with Na ranging from 0.54–1.58 wt%, Ca from 0.44–3.95 wt%, K from 1.19–3.06 wt%, Mg from 0.67–3.69 wt%, N from 0–0.75 wt%, and P from 0.21–1.34 wt%. In addition, the O/C ratios were lower than 1.0 and tended to decrease with increase in pyrolysis temperature. Surface functional groups on the biochar samples were determined qualitatively by FTIR and surface acid functional groups, phenolic, lactonic and carboxylic acids determined quantitatively showed little variation with pyrolysis temperature. These results indicate that the mesoporous melon seed shell-derived biochar could be used as an amendment for soil remediation.

1. INTRODUCTION

Melons are fruit plants that belong to the family of Cucurbitaceae with about 1,000 known species that are well-adapted to the warm tropics (Ogundare *et al.,* 2021). There are many varieties of melons with edible fruits, however, a few others with inedible fruits but with seeds of dietary and medicinal importance abound (Patel and Rault, 2017). *Citrullus colocynthis* is one of the species of melons that is widely cultivated in West Africa, the seeds of which are find use in food (Falade et al., 2020).

The processing for melon seeds for food generates a large quantity of melon seed shells (MSS), a post-harvest wastes that constitute environmental concern. The lignocellulosic nature of MSS presents a viable feedstock for the production of clean solid, liquid and gaseous biofuels. Several workers have explored the potential of biomass conversion technologies such as torrefaction (Nyakuma et al., 2014), pyrolysis and gasification techniques (Nyakuma et al., 2018) for valorizing agricultural wastes. Value addition to MSS via conversion technologies presents a practical effective and sustainable approach to MSS waste disposal and management.

The slow and incomplete combustion of biomass in inert or under limited oxygen conditions, at moderate temperatures (< 700^{o}C), pyrolysis is an effective method that can be used to convert large quantities of agricultural residues, such as MSS into solid biochar as main product with minor amount of gases and liquids. Temperature is a major factor influencing the outcome of the pyrolysis of lignocellulosic materials; the relative amount of the gaseous, liquid and solid products and the characteristics of the solid (biochar) produced. Several workers have reported on various aspects of the thermochemical treatment of MSS (Gao *et al.,* 2023 and Ahmed *et al.,* 2019) but the effect of pyrolysis temperature on the chemical and textural properties of the biochar produced pertinent to its use in diverse applications, such as amendment in contaminated soil remediation has not been widely reported.

The aim of the study is to pyrolyse melon seed husk (MSS) at different temperature and examine the associated chemical and textural properties may be useful in their application in soil remediation.

2. MATERIALS AND METHODS

2.1. Material Collection and Preparation of Samples

Melon seeds were purchased from local market in Benin City, Nigeria; and deshelled to obtain the melon seed shell (MSS). The MSS was air-dried, ground and sieved with a 200 µm mesh and a sub-sample were pyrolyzed in a Muffle furnace at 300, 350, 400 and 450 ^{o}C for 1 hr. respectively. The resulting biochar was labeled MSSB300, MSSB350, MSSB400 and MSSB450 respectively.

2.2. Characterization of the Biochar samples

The dry weight of the biochar was used to obtain yield. Dry combustion at 750 ^{o}C for 6 h was used for the determination of biochar ash content according to ASTM method (D175 284) which is recommended by the International Biochar Initiative which was described by Novak *et al.* (2009). The bulk density of the biochar sample was determined by the tapping method as described by Ahmedna et al. (2017). Nitrogen adsorption at 77 K was used to measure pore structure and biochar specific surface area using micrometric ASAP 202 and micrometric TriStar II 3020 (version 2.0). pH of biochar was determined according to the method described by Kun-yu *et al.* (2008) using a mixture of biochar to distilled water 1:10 v/v ratio. Boehm titration method was used to determine surface oxygen functional groups on the biochar (Boehm, 1994). FTIR analysis was carried out by using a Fourier transform infrared spectrophotometer (Bricker Fs 3v). The samples were mixed with KBr at a ratio of 1:100, compressed into a film and then scanned by FTIR spectrophotometer within the wavelength range 400 to 400 cm^{-1} (Wu et al., 2012). Scanning electron microscopy (SEM, Hitachi Sci 1500 scanning microscopy) was used to determine the surface morphology of the biochar sample. Electron dispersive X-ray (EDX) was used to determine the elemental composition of the biochar samples.

3. RESULTS AND DISCUSSION

3.1. Biochar Yield, Ash and Bulk density

Yield and ash contents of biochar samples at the different pyrolysis temperature, are given in Table 1. The results show that the biochar yield decrease (by about 2- fold) from about 56.64% for MSSB300 to

29.31% for MSSB450. This has been attributed to the increase rate of volatilization of organic components of the biomass with increase in pyrolysis temperature (Yang *et al.,* 2004). It can be seen from the results that similar to the trend in the values of yield that the ash content of the biochar samples decreased with increase in pyrolysis temperature (from 8.73% for MSSB300 to 7.93% for MSSB450). Elimination of the inorganic constituents of biomass associated with evolution of gases during pyrolysis is considered to be responsible for the observed reduction of about 9.71% in the ash content of the biochar samples. The results in Table 1 show that increase in pyrolysis temperature was associated with a decrease in the bulk density of biochar samples; The results suggest that fragmentation of cellulosic biomass followed by condensation and shrinkage of the resulting char during pyrolysis lead to increase in the density of the solid end-products (Demirbas, 2004). Bulk density is related to the aggregate nature of a materials with significant influence on porosity and fluid infiltration. Increase in the bulk density of biochar as indicated in Table 1 will tend to reduce its capacity to ameliorate the deleterious effect of the contaminants in polluted soil via reduced water infiltration and aeration. Therefore, biochar produced at lower temperature range (250 – 300 °C) may be more suitable amendment material than biochar samples produced at higher temperatures for the remediation of contaminated soil.

Table 1: Effect of pyrolysis temperature on yield, ash and bulk density of biochar sample

Parameters	MSSB300	MSSB350	MSSB400	MSSB450
Yield (%)	56.64	40.17	35.92	29.71
Ash (%)	8.73	7.58	9.12	7.93
Bulk density ($g.cm^{-3}$)	0.50	0.55	0.57	0.61

3.2. pH and Surface Acid Functional groups

The effect of pyrolysis temperature on pH and surface acid functional groups of biochar samples is given in Table 2. Biochar is usually a near neutral materials with pH in the range of 5 - 7.5 (Weber and Quicker, 2018). It can be seen from the result in Table 2 that increase in pyrolysis temperature was associated with increase in the pH of the biochar samples by 1.81 pH units from pH 7.36 for MSSB300 to pH 9.17 for MSSB450. The relatively high value pH of amendment material will result in a limiting effect when applied to soil with contaminant (Wu et al., 2018). The total surface acid functional groups on the biochar decreased from 3.55 $mmol.g^{-1}$ for MSSB300 to 3.05$mmol.g^{-1}$ for MSSB450. This moderate decrease (approx. 14.2%) is consistent with volatilization of surface groups, during pyrolytic decomposition of biomass (Yang *et al.,* 2004). Biochar surface functional groups are relevant to its sorptive properties capacity for ionic species.

Table 2: Variation of pH and surface acid functional groups of biochar with pyrolysis temperature

Parameters	MSSB300	MSSB350	MSSB400	MSSB450
pH	7.36	7.51	8.37	9.17
Carboxylic ($mmol.g^{-1}$)	3.55	3.50	3.35	3.05
Lactonic ($mmol.g^{-1}$)	1.15	1.20	1.35	1.08
Phenolic ($mmol.g^{-1}$)	1.27	0.90	0.27	0.18

3.3. Pore Properties of Biochar

Table 3 gives the variation of pore properties of biochar samples with temperature. The results in Table 3 show marked increase of about 81.40% in the surface area of biochars from 288.42 $m^2.g^{-1}$ for MSSB300 to 633.19 $m^2.g^{-1}$ for MSSB450. These results suggest that temperature is an important factor in the evolution of surface area of biochars and consistent to previous reports (Zhang *et al.,* 2015) and are collaborated with the observed mark increase of about 98.40% in the pore volume, from 0.183 $cm^3.g^{-1}$ for MSSB300 to 0.363 $cm^3.g^{-1}$ for MSSB450 (Table 3). The results (Table 3) indicate that the biochar samples prepared within the indicated temperature range are largely mesoporous (pore size > 2.0 nm). The relatively high specific surface area of the biochar samples together with the elaborate pore structures should enhance the adsorptive properties of the materials which are relevant to their soil application for the mitigation of mobility and availability of contaminants in soil.

Table 3: Effect of pyrolysis temperature on pore properties of biochar

Parameters	MSSB300	MSSB350	MSSB400	MSSB450
Surface area ($m^2.g^{-1}$)	288.42	355.36	472.28	633.91
Pore volume ($cm^3.g^{-1}$)	0.18	0.23	0.29	0.36
Pore size (nm)	2.43	2.41	2.42	2.11

3.4. FTIR of Biochar Samples

The FTIR spectra of the biochar samples in the range 500 - 4000 cm $^{-1}$ are shown in Figure 1. It can be seen that the absorption peaks that characterize the biochar samples are about the same but with difference in intensity are summarize in Table 4.

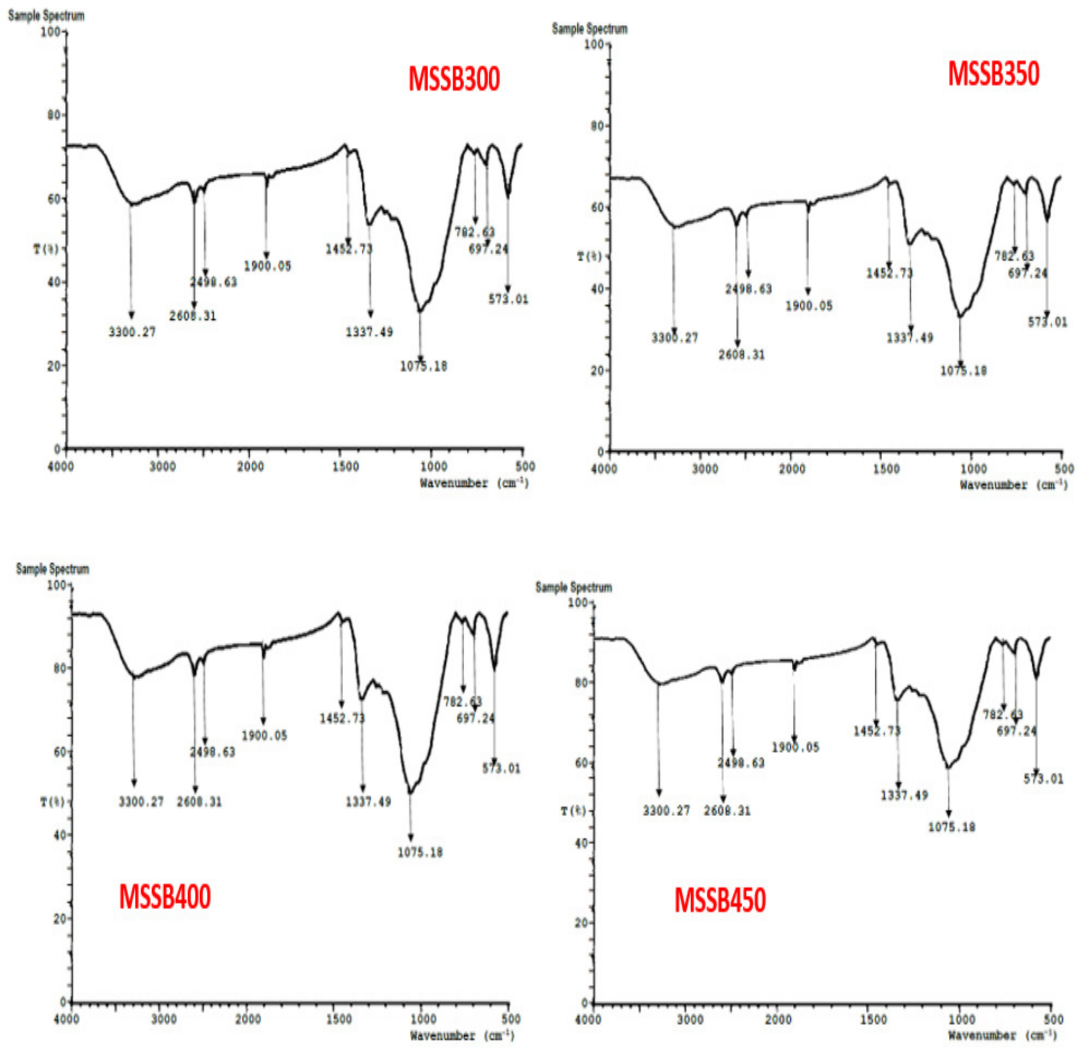

Figure 1: FTIR spectra of biochar samples prepared from MSS at different temperature

Table 4: FTIR absorption peak assignment of functional groups

Peak wavelength (cm^{-1})	Transmittance (%)	Assignment	Functional group
3300.27	60.13	O–H stretching vibration of inter and intramolecular hydrogen bonded phenols and carboxylic acids.	Hydroxyl group
2608.31	60.19	Aliphatic C–H stretching vibration	Carboxylic acid
2498.63	62.75	C=O stretching vibration of the carboxylic	Carboxylic acid
1900.05	64.38	C=O antisymmetric and symmetric stretching vibration in carboxylate groups	Carboxylic acid
1452.73	69.43	C–H in plane bending vibration of lignin	Alkanes
1337.49	55.41	C=C stretching vibrations	Alkenes
1075.18	32.65	C–OH vibrations of carboxylic acids and alcohol groups of cellulose	Alcohol
782.63	70.98	C=C–H vibration of benzene ring stretching vibrations	Alkenes
697.24	68.45	NH_2 and N–H stretching vibration	Amine
573.01	61.82	C–H stretching vibration	Alkanes

3.5. Surface Morphology and Elemental Composition of Biochar Samples

Scanning electron micrographs together with the Energy dispersive X-ray spectra of the biochar samples prepared at various pyrolysis temperature are shown in Figure 2. The surface morphology of the samples is seen to be porous, with increase in the pyrolysis associated with better evolution of the porous structure. Table 5 gives the elemental composition of the biochar samples prepared at various temperatures. The results in Table 5 show that increase in pyrolysis temperature is accompanied by an increase in the C content and decrease in the O content of the biochar samples and a concomitant in the in O/C ratios in the biochar samples. Volatilization of the non-carbon heat-labile moieties seemingly oxygen containing structures during pyrolysis leads to carbon enrichment of the residue, and thus in increase in O/C ratios with pyrolysis temperature (Gaskin et al., 2008). These results collaborate the observed increase in the bulk density of biochar samples with increase in pyrolysis temperature (Table 1). The results in Table 5 show that biochar samples contain alkaline elements. Na, Mg, Ca and K in various proportions, the amount of which tended to increase with pyrolysis temperature and varied in the order Ca < Na < K < Mg. These elements are important in maintaining alkalinity in soils and are of agronomic and environmental benefits. Aluminum and nitrogen both present in MSSB300 and MSSB350 appear to have been completely removed (volatilized) from MSSB400 and MSSB450 suggesting that these moieties may have been present in heat labile structures of biochar samples. The level of P, important in soil fertility and plant physiology, in the biochar samples decreased by about 20% from 0.46wt% in MSSB300 to 0.35wt% in MSSB450.

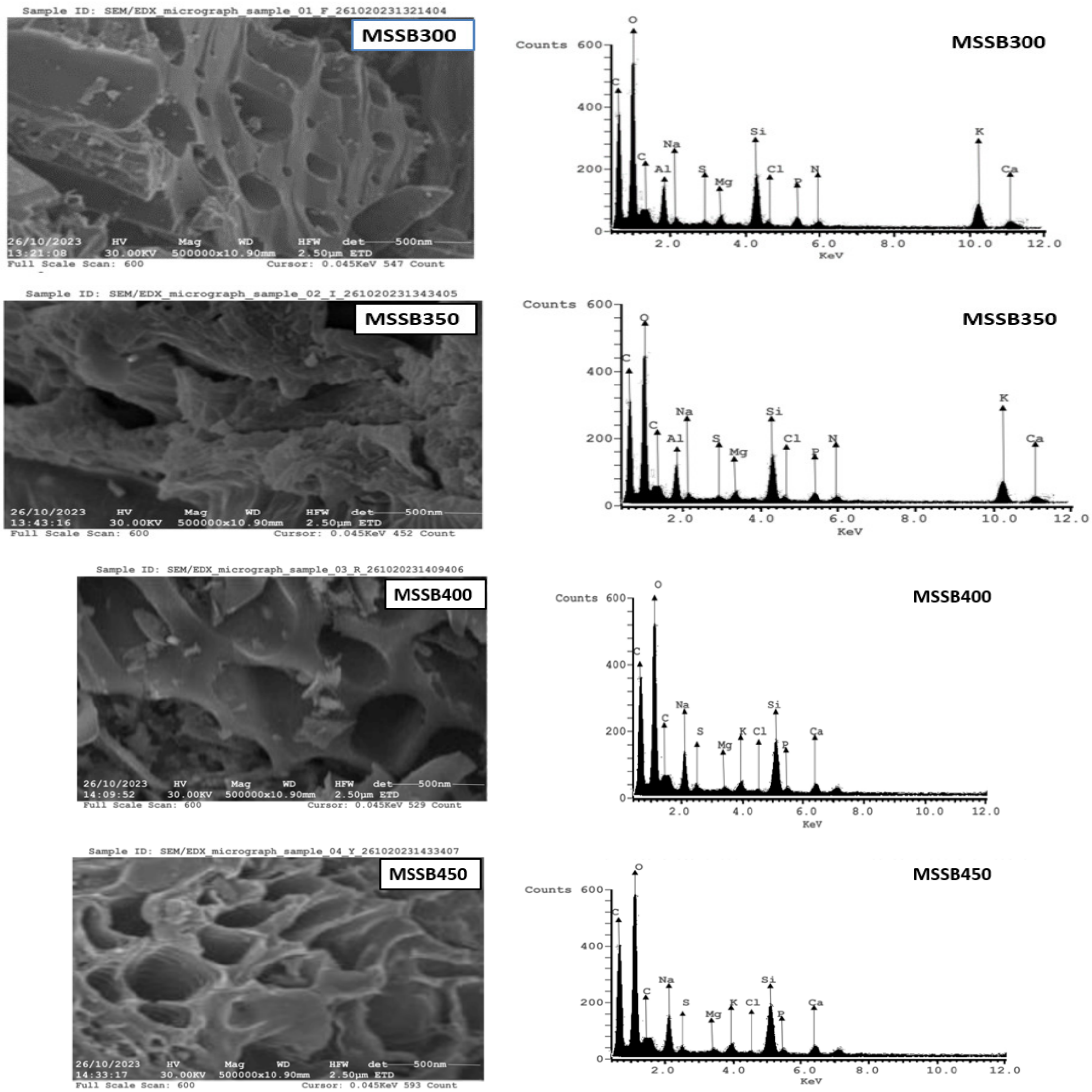

Figure 2: SEM and EDX of biochar prepared at various temperature

Table 5: Elemental composition of biochar samples prepared from melon seed husks at various temperature

Parameters	Compositions (wt %)			
	MSSB300	MSSB350	MSSB400	MSSB450
C	45.75	49.97	50.38	56.62
O	39.71	37.52	35.05	28.11
N	0.75	0.62	-	-
P	1.34	0.71	0.46	0.36
O/C	0.86	0.75	0.69	0.50
Ca	0.56	0.44	3.88	3.95
Na	1.58	0.98	0.54	0.83
Mg	2.30	0.67	3.14	3.69
K	1.19	2.62	3.06	3.01
P	0.46	1.34	0.21	0.35
Al	0.49	0.39	-	-
Si	6.73	4.46	2.31	2.71

4. CONCLUSION

The results from this study show that pyrolysis temperature has significant influence on the physicochemical, textural and pore structure characteristics of biochar that could influence agronomic and environmental benefits following soil application. Modeling to ascertain pyrolysis conditions, temperature, duration of heating and particle size of biomass precursor for attaining optimum biochar characteristics will be examined in further studies.

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