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Chemical characteristics of groundnut and sheanut shell biochars as adsorbents and soil conditioners in the era of ecological sustainability

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Abstract

This study investigated the influence of pyrolysis temperatures on characteristics of groundnut and sheanut shell biochars as potential adsorbents and soil conditioners. Groundnut and sheanut shell biochars were produced at pyrolysis temperatures of 350 ± 5 °C and 700 ± 5 °C using muffle furnace. The chemical characteristics of the biochars were analysed, potential contamination and ecological risk were determined based on the metal enrichment index and potential ecological risk index (PERI). pH values of the biochars ranged from 9.42 to 10.23 and 662.33 to 3206.67 $\mu\text{S}/\text{cm}$ for electrical conductivity. The total compositions of carbon and nitrogen for GB350, GB700, SB350 and SB700 ranged from 58.13% to 70.23% and 0.45% to 1.37%, respectively. The minerals composition of GB350, GB700, SB350 and SB700 ranged from 12944.92 to 20873.30 mg/kg for potassium, 192.24 to 410.72 mg/kg for sodium, 3567.98 to 13451.83 mg/kg for calcium and 1150.33 to 3414.34 mg/kg for magnesium. The pH of the biochars is found to be alkaline which upsurge with increasing pyrolysis temperature. Concentrations of nutrients such as calcium, potassium, magnesium and phosphorus diverse in groundnut shells feedstocks due to the pyrolysis conditions. The groundnut and sheanut shell biochars can increase essential nutrients such as nitrogen, phosphorus, and potassium in soil, which are conducive to growth of plant. The availability of phosphorus in the biochars make it phosphorus-rich and can be used as slow-release fertilisers. The potential toxic metals in the groundnut and sheanut shell biochars have values that suggested low contamination and less potential ecological risk making the biochars ecofriendly. Groundnut and sheanut shell biochars can be used in fields as an adsorbent and a soil amendment based on its chemical characteristics.

Keywords: Carbon, Essential nutrients, Groundnut shell biochar, Soil conditioners

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INTRODUCTION

Biochar is produced through slow pyrolysis process where organic material is heated in a complete or almost complete oxygen free environment to 300 °C to 700°C (Lehmann and Joseph, 2009). Biochar ability to adsorb pollutants varies depending on target pollutant and its physico-chemical properties (Ahmad *et al.*, 2014a). Adsorption process is influenced by numerous factors that play a vital role including the capacity of adsorption, surface area and mechanical stability (Khan *et al.*, 2020).

Biochar properties are more influenced by the feed stocks type or biomass than pyrolytic temperature. Hence, in designing a biochar for agricultural purpose, feed stock and pyrolysis temperature are the key factors to be carefully considered (Muhammad and Abdul, 2020). Temperature of pyrolysis has great influence on the structural, morphological, elemental and characteristics of biochars (Kołodyn'ska *et al.*, 2012). It is obvious that morphological and physico-chemical characteristics of biochars also depend on the nature of feed stock. Therefore, the main challenge is how to predict and produce a good biochar that will be agronomically acceptable, beneficial to soil and ecologically sustainable from any known feed stock by any given charring technology and production conditions (Hassnen *et al.*, 2020).

Biochar production is a cost-effective approach for recycling of waste due to the increasing price of disposal of waste (Pariyar *et al.*, 2020). The adaptation of this new method has aided farmers to better choose mineral and organic fertilisers and corresponding agronomic operations, so the soil can increase water retention capacity and provide higher yields, which results in enhanced water retention during droughts or extreme rainfalls, overall lessening the cost (Maroušek *et al.*, 2020). Soil fertility can be improved by biochar through the enhancement of the availability of essential nutrients for instance carbon, nitrogen and phosphorus (Zhang *et al.*, 2016).

Biochar has been generally referred as an eco-friendly soil amendment however harmful components (dioxins, environmentally persistent free radicals (EPFRs), heavy metals, perfluorochemicals (PFCs) and polycyclic aromatic hydrocarbons (PAHs)), may be produced owing to the preparation methods, preparation conditions, and unsuitable selection

of feedstocks (Xiang *et al.*, 2021). As a result of, its various interactions and potentially detrimental components with the environment, some researchers and scientists have taken interest in the negative effects of biochar on the environment (Cui *et al.*, 2021). Phytotoxicity of biochar research is mostly on germination experiments, which have some inadequacies, such as unclear internal mechanism, long experiment times, and other uncontrollable factors (Malfatti *et al.*, 2021). Godlewska *et al.* (2021) studied biochar potential environmental risks in soil (a single environmental medium); nevertheless, the biochar potential hazards on the atmosphere and waterbodies, in addition to the effects on diverse media are limited. Therefore, the overall potential risks of biochar application in soil, water, and the atmosphere must be comprehensively studied to determine the corresponding occurrence, detection, assessment, and avoidance measures of these risks.

Chemical characteristics information on biochar will help in its application in the environment, agriculture, nanotechnology and industry. Groundnut and sheanut shell in Ghana are usually burnt or left on the field to rot after harvesting. This can be recycled into biochar that have the potential of being used as an adsorbent for contaminant removal or immobiliser and as soil conditioners. Hence, this study investigated the influence of pyrolysis temperatures on groundnut and sheanut shell biochars and judged the chemical, elemental and nutrient composition that could serve as predictors of their suitability as potential adsorbent and soil conditioners. The potential of each feed stock to adsorb metals and as soil conditioners are discussed with respect to chemical properties, and conclusions are drawn on their suitability.

MATERIALS AND METHODS

Feed stocks and pyrolysis condition of biochar

Groundnut and sheanut shells were used to produce biochars (GB350 and GB700: groundnut shell biochar produced at pyrolysis temperatures of 350 ± 5 °C and 700 ± 5 °C, respectively; and SB350 and SB700: sheanut shell biochar produced at pyrolysis temperatures of 350 ± 5 °C and 700 ± 5 °C, respectively) in the Agricultural Sub-sector Improvement Programme (AgSsIP) Laboratory in the University for Development

Studies, Nyankpala Campus. The groundnut and sheanut shells were collected from Nyohini in the Tamale Metropolis. Foreign biomass and other materials were then removed from the feed stocks. Groundnut and sheanut shells were kept in earthen pots and then transferred into a Gallenkamp muffle furnace with internal dimensions of 18" x 8.5" x 7.5" High (1000 degrees centigrade, 220/40 volts, 16 amperes, H250). Gallenkamp muffle furnace was used to convert the feed stocks into biochar under a limited oxygen condition. The slow pyrolysis of groundnut shell biochar was produced at 350 ± 5 °C for 60 min and fast pyrolysis at 700 ± 5 °C for 45 min in a muffle furnace. The slow pyrolysis of sheanut shell biochar was produced at 350 ± 5 °C for 180 min and fast pyrolysis at 700 ± 5 °C for 90 min in a muffle furnace. The difference in residence time of pyrolysis of groundnut and sheanut shells are due to their difference in lignocellulosic biomass (Duwiejuah, 2017). After producing, the biochars were left to cool, crushed to fine powder, sieved through 0.2 mm and used for the chemical analysis.

Biochar chemical analysis

The biochars were produced in July, 2019 and phytocertification was obtained from Plant Protection and Regulatory Service Division (PPRSD) in Tamale, this aided in the transportation of the biochars samples to University of Reading, Department of Geography and Environmental Science, United Kingdom. Biochars were crushed and grinded to a homogeneous fine powder and dried up overnight at 105 °C preceding to ultimate analysis.

The pH was determined by weighing 10 g of biochar into a centrifuge tube (50 ml), and 25 ml ultra-pure water added using an automatic dispenser (BSI, 2005). The tube was capped and placed on a shaker for 15 minutes. A pH meter was used to determine the pH values of the biochar samples after the samples were kept for 30 min (BSI, 2005). Electrical conductivity was determined by weighing 10 g of air dried 2 mm sieved biochar into a centrifuge tube (50 ml), and 25 ml ultra-pure water added using an automatic dispenser (BSI, 2005). Samples of biochars were then kept for 30 min prior to measuring the EC values using a pre-calibrated conductivity meter (BSI, 2005).

Biochars analysis of C, N and S were conducted in triplicates using an elemental analyser (Flash *Bio-Research Vol.20 No.1 pp.1461-1472 (2022)*)

2000, CE Elantech Inc, New Jersey, USA) (Analytical Methods Committee, 2006). Colourimetric method was used to determine P in the extract (Wang *et al.*, 2012). Procedures involves extraction for K, Ca and Mg availability with 1 M HCl (Camps-Arbestain *et al.*, 2015).

Groundnut and sheanut shells biochars were milled, sieved, weighed into triangular glass bottles for the determination of Na and Fe contents and total concentrations (Al, Cu, Mn, Zn, Cd, Co, Cr, Ni and Pb). Approximately, 0.5 g of biochar was accurately weighed on a four-place balance using a plastic weighing boat (Alexander *et al.*, 2006). The biochar was then carefully transferred into a Kjeldahl digestion tube (100 ml). Carefully, nitric acid (10 ml concentrated) was added to each tube under a fume cupboard and a glass bubble then placed on top of the tube (Alexander *et al.*, 2006). They were then left in a fume cupboard overnight. The tubes were placed in the digestion block the next day and cautiously heated to 60 °C, left for 3 hours and gradually increased to 110 °C and digested for 6 hours (Alexander *et al.*, 2006). The tubes were removed from the block and were allowed to cool. The digestate was filtered using prewashed Whatman 540 filter papers (12.5 cm diameter) into a 100 ml volumetric flask, after which each volumetric flask was topped up with ultra-pure water to the mark. Dilution with water was done by a factor of two before running them on inductively coupled plasma optical emission spectroscopy (Alexander *et al.*, 2006). The apparent solutions were used to create the separate dilutions for Na and Fe compositions and total concentrations determination in groundnut and sheanut shells biochars using different standard instruments. Atomic absorption spectroscopy (C10G-E050B Shimadzu) was used to examine Na and Fe contents whereas inductively coupled plasma optical emission spectroscopy was used in the determination of Al, Cu, Mn, Zn, Cd, Co, Cr, Ni and Pb contents in the biochar. Samples were analysed for each parameter in the University of Reading, Department of Geography and Environmental Science, United Kingdom Laboratory.

Data analysis

Pearson correlations matrix of chemical parameters of the biochars were determined. The PERI (potential ecological risk index) proposed by Hakanson (1980) was used to assess the

potential ecological risk of potentially toxic elements in groundnut and sheanut shell biochars produced during slow and fast pyrolysis. The ecological sensitivity, toxic level, and total concentration to potentially toxic elements were taken into consideration by this method (Kabala and Singh, 2001). The potential ecological risk index was calculated following the various steps below Equations (1, 2, and 3):

$$C_f = \frac{C_m}{C_n} \dots\dots\dots \text{Eq 1}$$

$$E_r = T_r * C_f \dots\dots\dots \text{Eq 2}$$

$$R_i = \sum E_r \dots\dots\dots \text{Eq 3}$$

where C_f a measure of the degree of pollution on potentially toxic element is the contamination factor, C_m and C_n are the concentrations of each potentially toxic element in the mobile and stable fractions, respectively, biological toxic factor for each metal (5 for Cu, 1 for Zn, and 2 for Cr) is T_r (Hakanson, 1980); potential ecological risk index of individual element is E_r , and potential ecological risk index of the total pollution is PERI. The contamination factor, potential ecological risk and potential ecological risk index values (Table 1) were used to evaluate the risk of metals in the groundnut and sheanut shells biochars.

Table 1: Grading of C_f (contamination factor), the E_r (potential ecological risk coefficient) and PERI (potential ecological risk index)

C_f	E_r	PERI	Ecological risk
< 1	≤ 40	PERI ≤ 150	Low contamination
$1 < C_f \leq 3$	$40 < E_r \leq 80$	$150 < E_r \leq 300$	Moderate contamination
$3 < C_f \leq 6$	$80 < E_r \leq 160$	$300 < E_r \leq 600$	Considerable contamination
$6 < C_f \leq 9$	$160 < E_r \leq 320$	PERI > 600	High risk
$C_f > 9$	$E_r \geq 320$	-	Very high contamination

RESULTS AND DISCUSSION

The chemical properties of biochars produced during pyrolysis temperature of 350 ± 5 °C and 700 ± 5 °C were shown in Table 2. The pH values of groundnut and sheanut shells biochars ranged from 9.42 to 10.23 and 662.33 to 3206.67 $\mu\text{S/cm}$ for EC.

The temperature of pyrolysis affected the chemical characteristics and quality of biochar. The pH of groundnut and sheanut shell biochars tend to be alkaline and upsurge with increasing pyrolysis temperature. Biochar that are alkaline in nature can promote adsorption of toxic metals and metal hydroxide precipitation formation and can also improve acidic soil (Ahmad *et al.*, 2014b). Biochar has high immobilisation / removal abilities for toxic metals in soil / water as a result of its excellent surface chemistry, for example, different functional groups, high surface area, high aromaticity and high alkalinity (O'Connor *et al.*, 2018). A higher pH of biochars means they have more sites that are negatively charged for binding toxic metal ions from deprotonation of hydroxyl functional groups, which can lead to higher capacities of adsorption

(Mia *et al.*, 2017). The pH determines the charges on the surface of biochar (positives or negatives). The pH of circumneutral being the predominant charges are negative and can be used to remove cationic metals from contaminated water (Wongrod *et al.*, 2018). Similar studies, recorded pH values that ranged between 5 to 12 (Ahmad *et al.*, 2014b). Biochar produced with temperature increasing from 350 °C to 600 °C resulted in increasing pH from 9.11 to 10.35 (Shan *et al.*, 2020).

The EC for sheanut shell biochar produced during slow pyrolysis was < 750 $\mu\text{S/cm}$ implying the inadequacy of nutrient whilst groundnut shells biochar produced during slow pyrolysis was within the acceptable range of 750 to 2350 $\mu\text{S/cm}$. However, the groundnut and sheanut shells biochar produced during fast pyrolysis were in a range that is sensitive for tender plants, seedlings germination and can cause phytotoxicity. Understanding of the quantity of soluble salts biochar contain is paramount as high rates of its application to soil can adversely affect plants sensitive to salt (Joseph *et al.*, 2009) and phytotoxicity (Wilson *et al.*, 2001). Biochar electrical conductivity knowledge was essential for its applications in water, soil remediation and

agriculture. Production conditions and feed stock properties are the chief drivers of electrical conductivity of biochar (International Biochar Initiative, 2015). Electrical conductivity is dependent on the number of crystalline carbon structures, the porous structure and surface area

of biochar (Jiang *et al.*, 2013). It is related to water-soluble ions in the biochar (Rajkovich *et al.*, 2012), and it affects communities of soil microbes, plant growth, and soil physical properties, by this means incidentally influencing nutrient cycling of soil (Wang *et al.*, 2015).

Table 2: Chemical properties of biochars produced at pyrolysis temperature of 350 ± 5 °C and 700 ± 5 °C

Sample	GB350	GB700	SB350	SB700
pH	9.94 ± 0.21	10.23 ± 0.15	9.42 ± 0.13	9.94 ± 0.14
EC (µS/cm)	1481.00 ± 93.26	3206.67 ± 153.08	662.33 ± 50.29	3186.67 ± 128.97
%C	58.13 ± 1.10	63.47 ± 1.12	58.72 ± 1.19	70.23 ± 0.52
%N	1.37 ± 0.05	0.73 ± 0.03	0.74 ± 0.02	0.45 ± 0.03
S (mg/kg)	962.23 ± 19.95	780.66 ± 21.00	426.34 ± 8.38	247.91 ± 4.06
P (mg/kg)	1272.83 ± 9.02	1948.38 ± 24.73	903.72 ± 26.47	1298.34 ± 12.31
K (mg/kg)	16309.32 ± 145.49	20873.30 ± 320.86	12944.92 ± 166.18	19884.60 ± 215.45
Na (mg/kg)	328.11 ± 11.06	410.72 ± 2.25	192.24 ± 10.73	224.55 ± 3.31
Ca (mg/kg)	5586.87 ± 95.62	13451.83 ± 335.19	3977.29 ± 410.30	3567.98 ± 70.14
Mg (mg/kg)	2498.15 ± 44.24	3414.34 ± 68.15	1150.33 ± 25.27	1693.58 ± 32.09
Al (mg/kg)	1858.10 ± 32.23	4325.60 ± 7.42	1171.93 ± 159.23	1407.69 ± 16.77
Cu (mg/kg)	20.76 ± 0.66	27.23 ± 0.49	BDL	BDL
Fe (mg/kg)	9537.81 ± 321.79	10995.65 ± 182.74	6288.41 ± 1402.02	3487.03 ± 28.96
Mn (mg/kg)	170.07 ± 1.93	219.29 ± 3.22	119.16 ± 38.29	92.39 ± 4.20
Zn (mg/kg)	33.37 ± 0.69	32.20 ± 1.01	25.36 ± 0.57	27.18 ± 1.44
Cd (mg/kg)	BDL	BDL	BDL	BDL
Co (mg/kg)	1.62 ± 0.14	2.09 ± 0.12	1.41 ± 0.15	0.96 ± 0.22
Cr (mg/kg)	11.50 ± 0.63	14.70 ± 0.17	8.21 ± 3.12	5.51 ± 0.18
Ni (mg/kg)	BDL	BDL	BDL	BDL
Pb (mg/kg)	BDL	BDL	BDL	BDL

Note: BDL means below detection limits

The total compositions of C and N, for GB350, GB700, SB350 and SB700 ranged from 58.13% to 70.23% and 0.45% to 1.37%, respectively (Table 2). Maximum total carbon content was found in sheanut shell biochar produced during fast pyrolysis and lowest was found in groundnut shell biochar produced during slow pyrolysis. The low temperature pyrolysis (350 ± 5 °C) did not permit concentration of carbon in the groundnut and sheanut shell biochars hence the reason for less total carbon contents. During fast pyrolysis temperature, the groundnut and sheanut shell feed stocks yielded higher total carbon content that showed there was depletion of hydrogen and oxygen during the process of pyrolysis. Since, carbon content increased with increase in temperature of pyrolysis which is significant (Uzun and Apaydin-Varo, 2018). Similarly, high total content of corn straw and soybean biochars

were related to the O and H depletion during the process of pyrolysis (Zeng *et al.*, 2018). Biochar carbon content must be greater than 50% of the dry mass as organic matter pyrolysed with lower than 50% carbon content are categorised as PCM (Pyrogenic Carbonaceous Material) (European Biochar Certificate, 2012). In pyrolytic biochar, the proportion of carbon ranges from 50% to above 95% primarily depends on the feed stock instead of temperature of pyrolysis (Lu *et al.*, 2020). Similar studies found total content of 67.78% for corn straw biochar and 69.17% for soybean straw biochar (Sarfraz *et al.*, 2020), 64.50% to 75.30% for corn husk biochars produced at 600 °C and 500 °C, respectively (Sanka *et al.*, 2020) which are within the range of this present study. Recent studies that reported higher carbon content than this present study was Chen *et al.* (2020) and Khan *et al.* (2020).

Concentration of nitrogen is relatively very low in all the biochars which is attributable to the high temperature during the pyrolysis conditions. As, the organic material burning results in the loss of nitrogen as volatiles (NO_2 , N_2O and NH_3) from the feed stock (Sarfraz *et al.*, 2020). Similar study also reported low N content, 1.36% for BC600 and 1.11% for BC800 (Khan *et al.*, 2020) perhaps also due to N loss from the feed stock during pyrolysis at high temperature. The properties of biochar are in direct quantity to its unusual N content in the parent feed stock. Typically, legumes have additional N content in plant tissues (Sarfraz *et al.*, 2020). At large, high N content of biochar can provide soil nutrients and enhance crop productivity.

The heteroatoms composition of the GB350, GB700, SB350 and SB700 ranged from 247.91 to 962.23 mg/kg for S and 903.72 to 1948.38 mg/kg for P. The S concentration in GB350 and GB700 is relatively higher than SB350 and SB700. The finding of this study contrast that of Cheah *et al.* (2014) that reported that the amount of S is negligible in biochar. Phosphorus concentration in GB350, GB700 and SB700 are relatively higher and SB350 was lower in P content. Phosphorus content during the slow pyrolysis process can be preserved in feed stock. At higher temperatures, P is reserved in the biochar (Qambrania *et al.*, 2017). Biochar produced during low temperatures have additional soluble P that at high temperature becomes insoluble (Zheng *et al.*, 2013). Phosphorus in biochar is responsible for adsorption of toxic metal from aqueous solutions (Li *et al.*, 2017).

The mineral composition of the GB350, GB700, SB350 and SB700 ranged from 12944.92 to 20873.30 mg/kg for K, 192.24 to 410.72 mg/kg for Na, 3567.98 to 13451.83 mg/kg for Ca and 1150.33 to 3414.34 mg/kg for Mg (Table 2). Potassium concentration in GB700 and SB700 is fairly high which is far greater than GB350 and SB350. Sodium concentration in GB350 and GB700 are higher than SB350 and SB700. Calcium concentration in GB700 is relatively higher than GB350, SB350 and SB700 and showed significant difference between the biochars. Magnesium concentrations in GB350 and GB700 are relatively higher than SB350 and SB700. Similar study by Song and Guo (2012) found Ca, K, Mg and P content in poultry manure biochars to have increased by 32%, 31%, 30%,

and 34%, respectively, when temperature of pyrolysis increased from 300 °C to 600 °C.

Generally, the mineral content of groundnut and sheanut shell biochars increases with increasing temperature of pyrolysis. Mineral composition (Ca, Mg, K and P) in biomass and biochar, is also responsible for metal adsorption from aqueous solutions (Li *et al.*, 2017). Biochars with higher compositions of minerals can provide extra opportunities for toxic metals adsorption from water. Toxic metals are adsorbed onto the biochar via exchange mostly with Mg, K and Ca however with protons from hydroxyl and carboxyl groups. The minerals from feed stock biomass are not burned, so the pyrolysis process acts as a pre-concentration step of minerals. The pyrolysis conditions and variability in feed stock have a significant effect on the form and content of minerals in biochar (Zhao *et al.*, 2015). Hence, quantity of mineral in biochars can differ based on the original biomass composition and as a function of conditions of pyrolysis employed (Shen *et al.*, 2019).

The elemental concentrations in mg/kg of the GB350, GB700, SB350 and SB700 ranged from 1171.93 to 4325.60 for Al, 20.76 to 27.23 for Cu, 3487.03 to 10995.65 for Fe, 92.39 to 219.29 for Mn, 25.36 to 33.37 for Zn, 0.96 to 2.09 for Co and 5.51 to 14.70 for Cr whilst Cd, Ni and Pb were below detection limits (Table 2). Aluminum concentration in GB700 is relatively higher than GB350, SB350 and SB700. Copper was found only in groundnut shell biochars and was below detection limits in sheanut shell biochars. Iron concentration in GB350 and GB700 is relatively high which is far higher than SB350 and SB700. Manganese concentration in GB350 and GB700 was higher than SB350 and SB700. Similar study, found high concentration of 102.89 mg/kg for Mn and 85.07 mg/kg for Cu in biochar produced at 500 °C (Zhao *et al.*, 2017). Heteroatoms (for example N, O, P and S) are frequently present, whilst inorganic minerals (for example Ca, K, Mg, Na and Si) and some toxic elements (for example Al, As, Pb and Cd) may also be found in small quantities (Freddo *et al.*, 2012). With the exception of Na, K is the low valence metal ion which is more available than Ca, Al and Mg that are high valence metal ions in the groundnut and sheanut shell biochars. Some of the chemical parameters of the groundnut and sheanut shells biochars were correlated (Table 3).

Table 3: Correlation matrix for the chemical parameters of biochars

Parameter	pH	EC	N	C	Al	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Na	P	S	Zn
pH	1																
EC	0.746	1															
N	0.049	-0.490	1														
C	0.373	0.812	-0.757	1													
Al	0.704	0.572	-0.004	0.050	1												
Ca	-0.475	-0.635	0.507	-0.332	-0.848	1											
Co	0.370	0.071	0.334	-0.424	0.749	-0.487	1										
Cr	0.406	0.118	0.415	-0.436	0.783	-0.493	0.686	1									
Cu	0.683	0.288	0.532	-0.295	0.831	-0.413	0.799	0.836	1								
Fe	-0.498	-0.737	0.700	-0.599	-0.660	0.897	-0.312	-0.110	-0.192	1							
K	0.108	0.550	-0.635	0.891	-0.359	0.080	-0.719	-0.659	-0.567	-0.214	1						
Mg	0.834	0.558	0.281	-0.001	0.918	-0.593	0.719	0.770	0.951	-0.428	-0.334	1					
Mn	0.601	0.192	0.393	-0.310	0.777	-0.449	0.887	0.641	0.875	-0.353	-0.623	0.823	1				
Na	0.768	0.466	0.353	-0.101	0.898	-0.545	0.782	0.770	0.974	-0.384	-0.428	0.986	0.883	1			
P	0.849	0.775	-0.084	0.297	0.949	-0.800	0.602	0.639	0.783	-0.700	-0.088	0.931	0.688	0.887	1		
S	0.380	-0.126	0.851	-0.626	0.505	0.007	0.710	0.743	0.887	0.258	-0.728	0.710	0.743	0.773	0.414	1	
Zn	0.743	0.244	0.655	-0.246	0.582	-0.108	0.562	0.632	0.879	0.031	-0.383	0.832	0.729	0.835	0.617	0.846	1

Zinc concentration in GB350 and GB700 were a bit higher than SB350 and SB700. Cobalt concentration in GB350, SB350 and GB700 were a bit higher than SB700. Chromium concentration in GB350, SB350 and GB700 were a bit higher than SB700. Similar studies by Buss *et al.* (2016) established that the percentage availability of Cr, Ni, Cu and Zn increased with increasing temperature of pyrolysis.

Potentially, the groundnut and sheanut shell biochars can be used in fields as a soil amendment. They will improve the overall quality of soil. Biochar effect on the growth of plant is mainly related to different factors, for instance, biochar dosage rate, type of biochar, mixing depth, nutrients availability, soil texture and plant species (O'Connor *et al.*, 2018). The water holding capacity can be improved by addition of biochar into soil which helps in retention of water for a prolong period which is due to the highly porous structure of biochar (Liang *et al.*, 2006). In an irrigational situation, reducing the frequency and intensity of watering will reduce the cost. In acidic soil, biochar addition has led to an increase in pH of soil (Glaser *et al.*, 2002). Biochar addition in soil leads to increased cation exchange capacity which in turn lessens the nutrients loss through leaching (Lehmann, 2007). Since the biochar possess high CEC given it the ability to hold the nutrients available in the soil. As a result, it increases the use efficiency of nutrients in the soil which could have been washed away because of precipitation. Besides, the potential for groundnut and sheanut shell biochars to trap nutrients via CEC and can upsurge K content in the soil. Biochar increased the K availability in soils through the enhanced CEC (Gul and Whalen, 2016).

Nutrient contents (Ca, K, Mg and P) are diverse in groundnut and sheanut shells feed stocks due

to the pyrolysis conditions. These biochars can upsurge in soil essential nutrients (such as N, P and K), which are conducive for plant growth. Previous studies revealed that biochar can be used for supplying high quantities of Ca, K and Mg available to plants (Xu *et al.*, 2013). The availability of phosphorus in groundnut and sheanut shells biochars showed the biochars are P rich can be used as fertilisers. Hence, the nutrient-rich groundnut and sheanut shell biochars can be applied in arable soils as fertilisers. Application of biochar can improve content of nutrient, particularly of N. Biochar influence the available and total N in soil which is linked to ammonia volatilisation, organic N mineralisation and denitrification / nitrification (Gul and Whalen, 2016). It also increased efficiency of N utilisation by crops and reduced accumulation efficiency of N and then enhanced the N bioavailability in agricultural soils (Zheng *et al.*, 2013).

Potential ecological risk index

Copper, Cr and Zn in the groundnut and sheanut shell biochars recorded contamination factors values which were less than 1 (low contamination), potential ecological risk index value in the range of ≤ 40 and PERI below ≤ 150 (Table 4). The contamination factor of individual potential toxic elements measures the individual metals degree of pollution, and its value is indirectly proportional to its possible of leaching (Devi and Saroha, 2014). Copper, Cr and Zn all showed potential ecological risk index value below ≤ 40 (Table 4). The PERI measured the degree of superposition of several harmful potential toxic elements on the environment and organisms (Li *et al.*, 2013). The potential toxic metals in the groundnut and sheanut shell biochars have values that suggested low contamination and less potential ecological risk making the biochars ecofriendly.

Table 4: Contamination factor, potential ecological risk coefficient and potential ecological risk index of the groundnut and sheanut shells biochars produced during at $350 \pm 5^\circ\text{C}$ and $700 \pm 5^\circ\text{C}$

Biochar	C _f			E _r			PERI
	Cu	Zn	Cr	Cu	Zn	Cr	
GB350	0.42	0.19	0.13	2.08	0.19	0.26	2.52
GB700	0.54	0.18	0.16	2.72	0.16	0.33	3.21
SB350	0.00	0.14	0.09	0.00	0.09	0.18	0.27
SB700	0.00	0.16	0.06	0.00	0.06	0.12	0.18

CONCLUSION

Some chemical characteristics were dependent on temperature of pyrolysis and feed stock types. The mineral composition of biochars increases with increasing temperature of pyrolysis and will provide extra opportunities for toxic metals adsorption. The biochars can be used in fields as a soil amendment to enhance the overall quality of soil due to the high presence of total elements concentrations. They biochars can upsurge essential nutrients (N, P and K), in soil, which are conducive for growth of plant and can be used to release slowly fertilisers due to their richness in phosphorus. The potential toxic metals in the groundnut and sheanut shells biochars have values that suggested low contamination and less potential ecological risk making the biochars ecofriendly. Groundnut and sheanut shells biochars are promising feed stocks for water and soil remediation. Further research on some parameters and deeper understanding of their interactions between method of biochar production and feed stock is important to serve as guidelines for charring conditions and selecting feed stocks based to their specific environmental and soil requirements.

Conflict of Interest

Authors have no conflict of interest to declare

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AUTHOR CONTRIBUTIONS

DAB designed the study, carried out the research work and wrote the first draft of the manuscript. AA, QAK and AY reviewed the manuscript. All authors performed data analysis and interpretation and approved the final draft of the manuscript.

REFERENCES

Ahmad, M., Lee, S.S., Lim, J.E., Lee, S.E., Cho, J.S., Moon, D.H., Hashimoto, Y., and Ok, Y.S. (2014a). Speciation and

phytoavailability of lead and antimony in a small arms range soil amended with mussel shell, cow bone and biochar: EXAFS spectroscopy and chemical extractions. *Chemosphere*, **95**: 433 - 441.

Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S., and Ok, Y.S. (2014b). Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere*, **99**: 19 - 33.

Alexander, P.D., Alloway, B.J., and Dourado, A.M. (2006). Genotypic variations in the accumulation of Cd, Cu, Pb and Zn exhibited by six commonly grown vegetables. *Environmental Pollution*, **144**(3): 736 - 745.

Analytical Methods Committee (2006). Evaluation of analytical instrumentation. Part XIX. CHNS elemental analysers. *Accreditation and Quality Assurance*, **11**(11): 569 - 576. doi:10.1007/s00769-006-0185-x.

British Standards Institution (BSI). (2005). *BS ISO 10390: 2005 Soil quality. Determination of pH*.

Buss, W., Graham, M.C., Shepherd, J.G., and Masek, O. (2016). Risks and benefits of marginal biomass-derived biochars for plant growth. *Science of the Total Environment*, **569 – 570**: 496 - 506.

Camps-Arbestain, M., Amonette, J.E, Singh, B., Wang, T., and Schmidt, H.P. (2015). A biochar classification system and associated test methods. *In Biochar for Environmental Management: Science, Technology and Implementation. 2nd edn. (Eds J Lehmann, S Joseph) pp. 165 - 193.* Routledge, London.

Cheah, S., Malone, S.C., and Feik, C.J. (2014). Speciation of sulfur in biochar produced from pyrolysis and gasification of oak and corn stover. *Science of the Total Environment*, **48**: 8474 - 8480.

Chen, G., Wang, C., Tian, J., Liu, J., Ma, Q., Liu, B., and Lia, X. (2020). Investigation on cadmium ions removal from water by different raw materials-derived biochars. *Journal of Water Process Engineering*, **35**: 101223.

Cui, H., Li, D., Liu, X., Fan, Y., Zhang, X., Zhang, S., Zhou, J., Fang, G., and Zhou, J. (2021). Dry-wet and freeze-thaw aging activate endogenous copper and

- cadmium in biochar. *Journal of Cleaner Production*, **288**, 125605
- Deng, S., Chen, J., and Chang, J. (2021). Application of biochar as an innovative substrate in constructed wetlands/biofilters for wastewater treatment: performance and ecological benefits. *Journal of Cleaner Production*, **293**: 126156.
- Devi, P., and Saroha, A.K. (2014). Risk analysis of pyrolyzed biochar made from paper mill effluent treatment plant sludge for bioavailability and eco-toxicity of heavy metals. *Bioresource Technology*, **162**: 308 - 315.
- Ding, Z., Hu, X., Wan, Y., Wang, S., and Gao, B. (2016). Removal of lead, copper, cadmium, zinc, and nickel from aqueous solutions by alkali-modified biochar: batch and column tests. *Journal of Industrial and Engineering Chemistry*, **33**: 239 - 245.
- Duwiejuah, A.B. (2017). *Eco-friendly biochars for the adsorption of heavy metals from aqueous phase*. Master's thesis submitted in partial fulfilment of the requirements for degree of Master of Philosophy in Biotechnology in University for Development Studies.
- European Biochar Certificate (2012). *Guidelines for a sustainable production of biochar, European Biochar Certificate*. European Biochar Foundation, www.european-biochar.org, Accessed 1 January, 2021.
- Freddo, A., Cai, C., and Reid, B.J. (2012). Environmental contextualization of potential toxic elements and polycyclic aromatic hydrocarbons in biochar. *Environmental Pollution*, **171**: 18 - 24.
- Glaser, B., Lehmann, J., and Zech, W. (2002). Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal - a review. *Biology and Fertility of Soils*, **35**: 219 - 230.
- Godlewska, P., Ok, Y.S., and Oleszczuk, P. (2021). The dark side of black gold: ecotoxicological aspects of biochar and biochar-amended soils. *Journal of Hazardous Materials*, **403**: 123833.
- Gul, S., and Whalen, J.K. (2016). Biochemical cycling of nitrogen and phosphorus cycling in biochar-amended soils. *Soil Biology and Biochemistry*, **103**: 1 - 15.
- Hakanson, L. (1980). An ecological risk index for aquatic pollution control a sedimentological approach. *Water Research*, **14**: 975 - 1001.
- Hassnen, J., Zaid, H.M., and Anmar, D. (2020). Incorporating of two waste materials for the use in fine grained soil stabilization. *Civil Engineering Journal*, **6**(6): 1114 - 1123.
- International Biochar Initiative (2015). *Standardized product definition and product testing guidelines for biochar: That is used in soil [WWW Document]*. URL http://www.biocharinternational.org/sites/default/files/IBI_Biochar_Standards_V2.1_Final.pdf. (Accessed 12.25.21).
- Jiang, J., Zhang, L., Wang, X., Holm, N., Rajagopalan, K., Chen, F., and Ma, S. (2013). Highly ordered macroporous woody biochar with ultra-high carbon content as supercapacitor electrodes. *Electrochimica Acta*, **113**: 481 - 489.
- Joseph, S., Peacocke, C., Lehmann, J., and Monroe, P. (2009). *Developing a biochar classification and test methods*. In *Biochar for Environmental Management: Science and Technology*. 1st edn. (Eds J Lehmann, S Joseph) pp. 107 - 126. Earthscan, London.
- Kabala, C., and Singh, B.R. (2001). Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter. *Journal of Environmental Quality*, **30**: 485 - 492.
- Khan, Z.H., Gao, M., Qiu, W., Islam, M.S., and Song, Z. (2020). Mechanisms for cadmium adsorption by magnetic biochar composites in an aqueous solution. *Chemosphere*, doi: <https://doi.org/10.1016/j.chemosphere.2019.12.5701>.
- Kołodyn'ska, D., Wnętrzak, R., Leahy, J.J., Hayes, M.H.B., Kwapin'ski, W., and Hubicki, Z. (2012). Kinetic and adsorptive characterization of biochar in metal ions removal. *Chemical Engineering Journal*, **197**: 295 - 305.
- Lehmann, J. (2007). Bio-energy in the black. *Frontiers in Ecology and the Environment*, **5**(7), 381 - 387.
- Lehmann, J., and Joseph, S. (2009). Biochar for environmental management: An introduction. In *Biochar for Environmental Management, Science and Technology*; Lehmann, J., Joseph, S., Eds.; Earthscan: London, UK; p. 1 - 12.

- Li, F., Huang, J., Zeng, G., Yuan, X., Li, X., Liang, J., Wang, X., Tang, X., and Bai, B. (2013). Spatial risk assessment and sources identification of heavy metals in surface sediments from the Dongting Lake, Middle China. *Journal of Geochemical Exploration*, **132**: 75 - 83.
- Li, H., Dong, X., da Silva, E.B., de Oliveira, L.M., Chen, Y., and Ma, L. Q. (2017). Mechanisms of metal sorption by biochars: Biochar characteristics and modifications. *Chemosphere*, **178**: 466 - 478.
- Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J.O., Thies, J., Luizão, F.J., Petersen, J., and Neves, E.G. (2006). Black carbon increases cation exchange capacity in soils. *Soil Science Society of America Journal*, **70**: 1719 - 1730.
- Lu, L., Yu, W., Wang, Y., Zhang, K., Zhu, X., Zhang, Y., Wu, Y., Ullah, H., Xiao, X., and Chen, B. (2020). Application of biochar-based materials in environmental remediation: from multi-level structures to specific devices. *Biochar*. <https://doi.org/10.1007/s42773-020-00041-7>.
- Malfatti, Ad.L.R., Mallmann, G.C., Oliveira Filho, L.C.I., Carniel, L.S.C., Cruz, S.P., and Klauberg-Filho, O., 2021. Ecotoxicological test to assess effects of herbicides on spore germination of *Rhizophagus clarus* and *Gigaspora albida*. *Ecotoxicology and Environmental Safety*, **207**, 111599.
- Maroušek, J.P., Bartoš, M., Filip, L., Kolář, P., Konvalina, A., Maroušková, J., Moudrý, J., Peterka, J., Šál, J., Šoch, M., Stehel, V., Strunecký, O., Suchý, K., Vochozka, M., Vrbka, J., and Zoubek, T. (2020). Advances in the agrochemical utilization of fermentation residues reduce the cost of purpose-grown phytomass for biogas production. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, **1** - 11. doi: 10.1080/15567036.2020.1738597.
- Mia, S., Singh, B., and Dijkstra, F.A. (2017). Aged biochar affects gross nitrogen mineralization and recovery; A 15 N study in two contrasting soils. *Glob Change Biology Bioenergy*, **9**: 1196 - 1206.
- Muhammad, J.M., and Abdul, R.M. (2020). Wheat straw optimization via its efficient pretreatment for improved biogas production. *Civil Engineering Journal*, **6**(6): 1056 - 1063.
- O'Connor, D., Peng, T., Zhang, J., Tsang, D.C.W., Alessi, D.S., Shen, Z., Bolan, N.S., and Hou, D. (2018). Biochar application for the remediation of heavy metal polluted land: a review of in situ field trials. *Science of The Total Environment*, **619-620**: 815 - 826.
- Pariyar, P., Kumari, K., Jain, M.K., and Jadhao, P.S. (2020). Evaluation of change in biochar properties derived from different feedstock and pyrolysis temperature for environmental and agricultural application. *Science of the Total Environment*, **136433**. doi:10.1016/j.scitotenv.2019.136433.
- Qambrania, N.A., Rahmana, M., Wonc, S., Shima, S., and Raa, C. (2017). Biochar properties and eco-friendly applications for climate change mitigation, waste management, and wastewater treatment: A review. *Renewable and Sustainable Energy Review*, **79**: 255 - 273.
- Rajkovich, S., Enders, A., Hanley, K., Hyland, C., Zimmerman, A.R., and Lehmann, J. (2012). Corn growth and nitrogen nutrition after additions of biochars with varying properties to a temperate soil. *Biology and Fertility of Soils*, **48**: 271 - 284.
- Sanka, P.M., Rwiza, M.J., and Mtei, K.M. (2020). Removal of selected heavy metal ions from industrial wastewater using rice and corn husk biochar. *Water Air Soil Pollution*, **231-244**: 1 - 13.
- Sarfaraz, Q., Silva, L., Drescher, G., Zafar, M., Severo, F., Kokkonen, A., Molin, G., Shafi, M., Shafique, Q., and Solaiman, Z. (2020). Characterization and carbon mineralization of biochars produced from different animal manures and plant residues. *Scientific Reports*, **10**(955): 1 - 9.
- Shan, R., Shi, Y., Gu, J., Wang, Y., and Yuan, H. (2020). Single and competitive adsorption affinity of heavy metals toward peanut shell-derived biochar and its mechanisms in aqueous systems. *Chinese Journal of Chemical Engineering*, <https://doi.org/10.1016/j.cjche.2020.02.012>.

- Shen, Z.T., Hou, D.Y., Jin, F., Shi, J.X., Fan, X.L., Tsang, D.C.W., and Alessi, D.S. (2019). Effect of production temperature on lead removal mechanisms by rice straw biochars. *Science of the Total Environment*, **655**: 751 - 758.
- Song, W., and Guo, M. (2012). Quality variations of poultry litter biochar generated at different pyrolysis temperatures. *Journal of Analytical and Applied Pyrolysis*, **94**: 138 - 45.
- Uzun, B.B., and Apaydin-Varo, E. (2018). Potentials to mitigate climate change using biochar: Turkey's perspective, Forebiom Country Case report Turkey. *IUFRO Occasional Papers*, **27**: 1 - 8.
- Wang, T., Camps-Arbestain, M., Hedley, M., and Bishop, P. (2012). Predicting phosphorus bioavailability from high-ash biochars. *Plant and Soil*, **357**: 173-187. doi:10.1007/s11104-012-1131-9.
- Wang, Y., Lin, Y., Chiu, P.C., Imhoff, P.T., and Guo, M. (2015). Phosphorus release behaviors of poultry litter biochar as a soil amendment. *Science of the Total Environment*, **512**: 454 - 463.
- Wilson, S.B., Stoffella, P.J., and Graetz, D.A. (2001). Use of compost as a media amendment for containerized production of two subtropical perennials. *Journal of Environmental Horticulture*, **19**(1):37- 42.
- Wongrod, S., Simon, S., Guibaud, G., Lens, P.N.L., Pechaud, Y., Huguenot, D., and van Hullebusch, E.D. (2018). Lead sorption by biochar produced from digestates: consequences of chemical modification and washing. *Journal of Environmental Management*, **219**: 277 - 284.
- Xiang, L., Liu, S., Ye, S., Yang, H., Song, B., Qin, F., Shen, M., Tan, C., Zeng, G., and Tan, X. (2021). Potential hazards of biochar: The negative environmental impacts of biochar applications. *Journal of Hazardous Materials*, **420**: 126611.
- Xu, X.Y., Cao, X.D., Zhao, L., Wang, H., Yu, H., and Gao, B. (2013). Removal of Cu, Zn, and Cd from aqueous solutions by the dairy manure-derived biochar. *Environmental Science and Pollution Research*, **20**: 358 - 368.
- Zeng, X., Xiao, Z., Zhang, G., Wang, A., Li, Z., Liu, Y., Wang, H., Zeng, Q., Liang, Y., and Zou, D. (2018). Speciation and bioavailability of heavy metals in pyrolytic biochar of swine and goat manures. *Journal of Analytical and Applied Pyrolysis*, **132**: 82 - 93.
- Zhang, G., Guo, X., Zhao, Z., He, Q., Wang, S., Zhu, Y., Yana, Y., Liu, X., Sun, K., Zhao, Y., and Qiana, T. (2016). Effects of biochars on the availability of heavy metals to ryegrass in an alkaline contaminated soil. *Environmental Pollution*, **218**: 513 - 522.
- Zhao, L., Cao, X., Zheng, W., Wang, Q., and Yang, F. (2015). Endogenous minerals have influences on surface electrochemistry and ion exchange properties of biochar. *Chemosphere*, **136**: 133 - 139.
- Zhao, S., Ta, N., and Wang, X. (2017). Effect of temperature on the structural and physicochemical properties of biochar with apple tree branches as feedstock material. *Energies*, **10**: 1 - 15.
- Zheng, H., Wang, Z., Deng, X., Zhao, J., Luo, Y., Novak, J., Herbert, S., and Xing, B. (2013). Characteristics and nutrient values of biochars produced from giant reed at different temperatures. *Bioresource Technology*, **130**: 463 - 471.