International Journal of Advanced Research and Publications
ISSN: 2456-9992

“Impact Of Pyrolysis Temperature And Biomass Type On Physicochemical Properties Of Biochar On Soil Fertility”

Innocent Igiraneza, Protogene Hakizimana, Immaculee Bayisenge

University of Rwanda , College of Science and Technology
P.O. Box : 4285, Kigali- Rwanda , +250781939580
innocentigiraneza04@gmail.com

University of Rwanda , College of Medecine and Health Sciences
P.O. Box : 4285, Kigali- Rwanda , +250788282971
prokist2014@gmail.com

University of Lay Adventist of Kigali,
P.O. Box : 6392, Kigali- Rwanda , +250780367899
bayisengeimmaculee@gmail.com

Abstract: Biochar is pyrogenous, organic material synthesized through pyrolysis of different biomass (plant or animal). Main biochar applications include: pollution remediation due to high CEC and specific surface area, soil fertility improvement and carbon sequestration due to carbon and ash content etc. Pyrolysis temperature and biomass type used to prepare biochar affect the physicochemical characteristics of produced biochar, and when applied as soil amendment shows a range of results. In this study, Different biochars were prepared from different biomass types, namely Corn cobs (Zea mays), eucalyptus tree branches (Eucalyptus globulus), potato peels (Solanum tuberosum) at and sorghum tassels (Sorghum bicolor) at temperature range of 600^0C-700^0C. However, eight biochars were prepared where four biochars were prepared in open environment and other in furnace. The impact of temperature and biomass type on variability of physicochemical characteristics of obtained biochars were evaluated through measuring pH, electrical conductivity(EC), total dissolved solids and moisture content and Moreover, the physicochemical properties of biochar determine application of this biomaterial as an additive to improve soil fertility. The objective of study was to evaluate the impact of biomass type and pyrolysis temperature on physicochemical properties of biochar on soil fertility. The results of moisture content of different biomass types, namely Corn cobs (Zea mays), eucalyptus tree branches (Eucalyptus globulus), potato peels (solanum tuberosum) and sorghum tassels (Sorghum bicolor) are 59.97$\pm\mathbf{0.03}\%, \mathbf{39.87 \pm 0.03}\%, \mathbf{79.65 \pm 0.04}\%$ **and** $\mathbf{23.75 \pm 0.03}\%$respectively. The pH in furnace was :9.90, 10.03, 9.95, 10.03 respectively; EC :1850, 1248, 4660, 5400; TDS:989, 651, 2630, 3110 respectively and in open environment was :11.20, 11.06, 10.04, 11.92; 2640, 2630, 7590, 5720; 1401, 1407, 4260, 320 in pH, EC, TDS respectively.All results reported with negative values are not detected in samples (ND)

Key words: Biomass type, Electrical Conductivity (EC), moisture content , Total Dissolved Solid (TDS) and hydrogen potential (pH).

1. Introduction

Pyrolysis of biomass such as wood, manure or leaves in presence of an inert gas with limited or no air results in a carbon rich product called biochar. It can be used not only as renewable fuel, but also as an additive for improvement of soil quality. The nature of carbon structures is the key reason for its high stability. The chemical difference between biochar and other organic matter is its higher proportion of aromatic C and condensed aromatic structures, in contrast to other aromatic structures of soil organic matter, such as lignin. The condensed aromatic structure of biochars can have varying forms, including amorphous C (which dominates at lower pyrolysis temperatures), turbostratic C (formed at higher temperatures) and graphite C(Tomczyk, 2020) The beneficial effects of biochar were discovered more than 2, 000 years ago when the “slash and burn” agricultural method was in practice. Natural forest fires and historical cultural practices also resulted in the formation of biochars that are stable over thousands of years as soil deposits. There are numerous types of biochars depending on the biomass types from which they are derived. Each biomass type results in a very specific and different type of biochar, reflecting the physicochemical properties of the original biomass type. For example, biochars made from different types of trees or plant species result in different types of biochars (Hunt et al., 2010). The reason why biochar gained public interest is mainly associated with its carbon sequestration ability which reduces the atmospheric CO_2 concentration. The half-life of biochar in the soil is estimated to range from hundreds to thousands of years. Therefore, supplying the soil with biochar is a strategy for long-term carbon sequestration. Moreover, there is increasing interest in biochar as a soil amendment. Number of studies has demonstrated that biochar application can significantly improve crop productivity, improve soil conditions, and increase the efficiency of fertilizers and also used in remediation processes(Glodowska & Cultivation, 2017). Below figure indicates the condensed aromatic structures of biochars with varying forms due to different temperatures at which they are produced(Tomczyk, 2020).

2. MATERIALS AND METHODS

2.1. Sampling and sampling site

Four different biomass types namely Corn cobs (Zea mays), eucalyptus tree branches (Eucalyptus globulus), potato peels (Solanum tuberosum) and sorghum tassels (Sorghum bicolor) were collected in Kimonyi, Musanze, Rwanda at geologic location of $1^0 29^{'} 39.6^{''}$S $29^0 37^{'} 21.4^{''}$E. However, soil sample were collected in Nyabugogo wetland located in Gasabo district in Kigali city at geologic location of $1^0 56^{'} 17.23524^{''}$S $30^0 2^{'} 41.04168^{''}$E.

Figure 1: *Biomass types (Eucalyptus globules, Sorghum bicolor, Solanum tuberosum and Zea mays)*

2.2. Moisture content determination of the samples

40 g of each fresh sample were measured with an electronic balance and put in oven setted at $105^{0}C$ for drying and as a means to determine moisture content of our samples. However, moisture content was determined as a percentage of a ratio of difference in masses of samples before put in the oven and the samples from the oven over mass before putting the samples in the oven.

2.3. Determination of Physicochemical properties of biochars

1) 2.3.1. pH, TDS and EC

Biochar samples (including four prepared in open environment and other four biochars prepared in furnace) were mixed with distilled water at the ratio of 1:5 (wt:vol) and shaked for 2 min. After letting the mixture for 1 h, the PH, TDS and EC of the mixture was measured using electrochemical probe (R. Zhao et al., 2015). However, pH of soil sample was measured by using the same way. Additionally, above biochars were mixed with soil sample in ratio of 1:3 (bio:soil) and pH was measured after about a day in order to see their different effects on pH of this soil sample.

2.3.2. Surface functional groups

The surface functional groups were determined by dissolving biochar samples (including four prepared in open environment and other four biochars prepared in furnace) with ethanol solvent in ratio of 1:10 (bio:ethano) and shaken for 2 min. The mixture was kept about a day for easy decantation and filtration. The obtained liquid after filtration was analysized on FTIR.

2.4. Bulk density of soil

Bulk density of soil is the measure of particles contained in a unit volume of dry soil including pore spaces. Bulk density indicates how tightly the soil particle is packed (soil compaction). The critical value of bulk density for restricting root growth varies with soil type but in general bulk densities greater than 1.6 g/cm3 tend to restrict root growth. In clay soils with good soil structure, there is a greater amount of pore space because the particles are very small, and many small pore spaces fit between them. Sandy soils usually have higher bulk densities (1.6–1.8 g/cm3) than fine silts and clays (1.1 – 1.6 g/cm3) because they have larger, but fewer, pore spaces (Gardi et al., 2002). Generally, bulk density of soil is calculated as the dry weight of soil divided by its volume. Therefore, in our practice bulk density was calculated by measuring the weight of container with soil sample minus the weight of an empty container divided by volume of quantity of water that filled the used empty container so, this volume was equal to volume of soil sample that filled that container too. The following formula was used.

$BD = \frac{W_2 - W_1}{V}$ *, where* W_2 *is weight of container with soil,* W_1 *is weight of empty container and V is volume of soil*

2.5. Heavy metals adsorption property of biochars

Biochar has a large surface area, and high capacity to adsorb heavy metals and organic pollutants. Biochar can potentially be used to reduce the bioavailability and leachability of heavy metals and organic pollutants in soils through adsorption and other physicochemical reactions(Zhang et al., 2013). For this assessment, biochar samples (including four prepared in open environment and other four biochars prepared in furnace) were mixed with soil sample in ratio of 1:3 (bio:soil) and then 40 mL of distilled water were added in the each beaker. The mixtures were shaken for 5 min and left for overnight for easy decantation and filtration. However, after filtration three drops of nitric acid (HNO_3) were added in each beaker in fumehood and then left them for two hours for digestion before measuring heavy metals on AAS. Moreover, nitric acid (HNO_3) was used because of its strong oxidizing ability and two hours were used in order to increase exothermic reactions which increase the extent of solubilization of the metals of the interest from soil matrix as well as loss of these metals through volatilization(Mohammed et al., 2017).

Figure 2: *Mixture of biochar with soil before filtration*

Figure 3: *Mixture of biochar with soil after filtration*

In addition, external calibration was used in order to determine unknown concentrations of heavy metals from absorbance given by AAS. Therefore, standard solutions of 5ppm, 2ppm, 1ppm, 0.5ppm, 0.1ppm and 0.05ppm of Cu, Mn, Iron, Zn and Cd were prepared in volumetric flask of 200mL from stock solution of 1000ppm. The volume of stock solution required was calculated by the aid of this formula $C_1V_1= C_2V_2$, where C_1 is the concentration of stock solution, V_1 is the volume of stock solution required, C_2 is the concentration of standard and V_2 is the volume of the standard. However, the volume of stock solution calculated was measured by volumetric cylinder before it was poured in 200mL volumetric flask containing 5% nitric acid for digestion where distilled water was added up to the mark of the flask and the mixture were left for two hours for digestion to be completed.

3. RESULTS AND DISCUSSIONS

3.1. Moisture content determination of the samples

Four samples of corn cobs, eucalyptus tree branches, potato peels and sorghum tassels were weighed and put in oven at 105^0C for moisture content determination after they are dried and the results were recorded in the following table.

Table 1: *Results of moisture content from samples of different biomass types*

Biomass type	Moisture content (%)
Corn cobs	59.97 ±0.03
Eucalyptus tree branches	39.87 ±0.03
Potato peels	79.65 ±0.04
Sorghum tassels	23.75 ±0.03

The resulting moisture content for our samples were different because biomass types were different and they had different chemical and physical nature. However, biomass with low moisture content resulted into high amount of biochar while biomass with high moisture content produced low amount of biochar. In brief, biomass type with low moisture content requires low energy for its pyrolysis and produces high amount of biochar with quality, good yield and low emissions(Joseph, S. Taylor, 2019).

3.2. Determination of physicochemical properties of the biochars

3.2.1. pH, EC and TDS

Table 2: *Physicochemical properties of biochars prepared in furnature*

Biochar type	pH	EC (µS/cm)	TDS (mg/L)
Corn cobs	9.90	1850	989
Eucalyptus tree branches	10.03	1248	651
Potato peels	9.95	4660	2630
Sorghum tassels	10.03	5400	3110

Table 3: *Physicochemical properties of biochars prepared in Open environment*

Biochar type	pH	Conductivity(µS/cm	TDS (mg/L)
Corn cobs	11.20	2640	1401
Eucalyptus tree branches	11.06	2630	1407
Potato peels	10.04	7590	4260
Sorghum tassels	11.92	5720	3200

Biochar is usually produced under limited or no oxygen conditions in order to avoid the oxidation of carbon present in the feedstocks/biomass. For feedstocks/biomass pyrolyzed in the presence of oxygen this carbon is oxidized. Therefore, this oxidation of carbon converts biomass into ash and loss of almost all the aromatic compounds and nutrients except minerals(Singh et al., 2017). So, this is the reason why we obtained high pH towards basic region, electrical conductivity and total dissolved solids for biochar prepared in open environment where, there is high oxygen content as result of high ash content. Moreover, for biochars prepared in furnace there were low pH, electrical conductivity and total dissolved solids because they were made in limited oxygen conditions which led to low oxidation of carbon in feedstocks, low ash content and some aromatic compounds are retained compared to those from open environment. In addition, biomass type also affected the values of pH, electrical conductivity and total dissolved solids and that is why for instance, electrical conductivity of biochar made from potato peels in furnace is greater than for those of biochar made from corn cobs in open environment. As conclusion, open/high oxygen firing becomes a kind burning and resultant product (least carbon compound or ash and soot particles) would not be having the properties same as biochar so, it is advisable to prepare biochar in limited oxygen conditions.

3.2.2. Surface functional groups

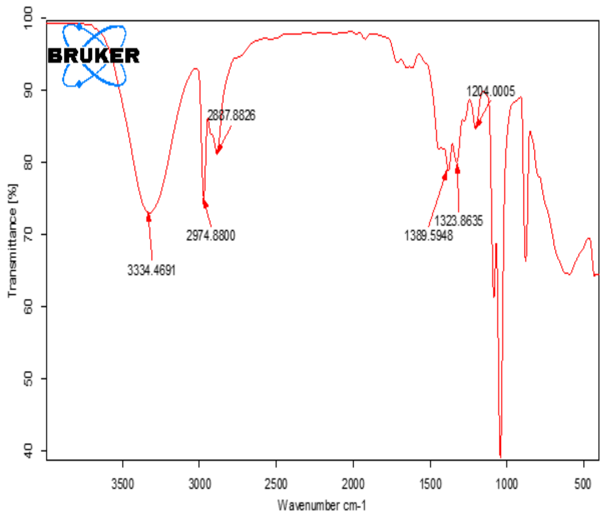


Figure 4: *Infra red spectrum for biochar*

From above spectrum the vibration band centred at 3334.4691cm^{-1} is attributed to the presence of O-H groups stretching (alcohols and phenols), vibration bands of the range of 2974.8800 cm^{-1} and 2887.8826 corresponds to C-H stretching of alkanes, vibration band at 1389.5948 cm^{-1} corresponds to C-H bending, vibration band at 1323.8635 cm corresponds to N-O groups or nitro-groups and band centred at 1204.0005 cm^{-1} is attributed to the presence of C-O-C groups and aryl groups. For all biochars we got the same spectrum and this is addressed to the factor that during preparation of them all biomasses were applied to the same range of temperature of 600^{0}C- 700^{0}C and this range was chosen as the biochars produced at this range has high pH and high metal adsorption efficiency due to a reduction in the amounts of negative surface charges related to functional groups such as –COOH, –COH and –OH (J. J. Zhao et al., 2019). Therefore, these are important factors for biochar to increase soil fertility and for remediation of metal contaminated soil. Moreover, some functional groups like carboxyl and carbonyl groups were observed because at this range of temperature, they are degraded.

3.3. Effect of biochar on soil pH

For this purpose, pH of soil without biochar was determined and it was 8.25. Thereafter, pH also was determined after putting different biochars in soil sample in order to see the biochar effect on soil pH. Obtained results are in the table below. Biochar type indicates a solution of biochar and soil.

Table 4: *Results of soil pH after exposure to different biochars*

Biochar type	Furnace (pH)	Open environment (pH)
Corn cobs	9.95	8.38
Eucalyptus globules	9.02	8.43
Potato peels	8.92	8.56
Sorghum tassels	10.03	8.60

From obtained results, soil pH increased after biochar was added. However a great increase was observed for biochars made from furnace, this indicate that there was high biochar-soil interactions for biochars made from furnace than those made from open environment. Biochar increase of soil pH is important because almost all crops grow better in basic medium than in acidic medium therefore, soil acidity reduces the soil fertility. There are many mechanisms that enable biochar to prevent the acidity of the soil and help to increase the soil pH. Biochar‶s specific properties reduce the soil acidity through its alkaline nature and high buffer capacity. The ability of biochar particles to absorb the H+ ions, as well as decarboxylation processes, are probably the main factors in soil acidity neutralization(Juriga & Šimanský, 2019). During pyrolysis, the cations such as Ca, Mg, K and Si which are contained in organic materials used in bio-fuel production, form carbonates or oxides. When biochar are applied to acidic soil, these carbonates and oxides react with H$^+$ and Al^{3+} ions in the soil and then lead to increase of soil pH or the alkalinity of soil and decrease the soil's acidity. However, the range of changes in pH and acidity depends on biochar properties(Juriga & Šimanský, 2019).

$$CaCO_3(s) + H_3O^+ (aq) \rightarrow Ca^{2+} (aq) + HCO_3^- (aq) + H_2O (l)$$

$$2NaAlSi_3O_8(s) + 2H^+(aq) + 9H_2O(l) \rightarrow 2Na^+(aq) + Al_2SiO_4(OH)_4(s) + 4H_4SiO_4(s)$$

$$NaAlSiO_8(s) + H^+(aq) + 7H_2O(l) \rightarrow Na^+(aq) + Al(OH)_3(s) + 3H_4SiO_4(s)$$

B. 3.4. Effect of biochar on soil bulk density

The bulk density of soil without biochar was calculated and then also calculated after adding different biochars in soil. The results were recorded in the following table.

Table 5: Bulk density of biochar amended soil

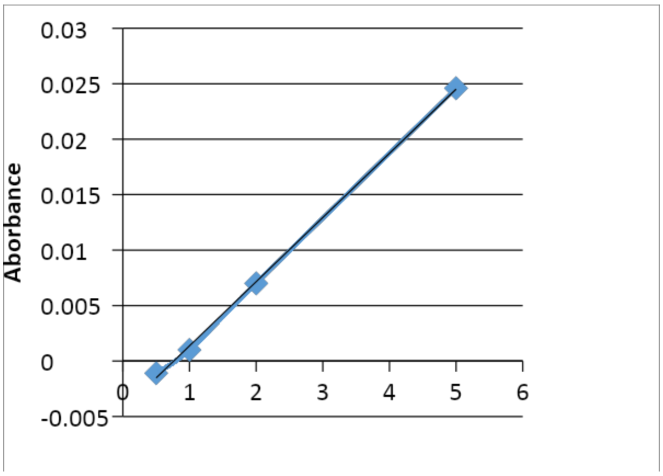
Biochar type	Furnace (bulk density/mg/mL)	Open environment (bulk density/mg/mL)
Corn cobs	0.96	0.87
Eucalyptus globules	0.99	0.96
Potato peels	1.07	0.98
Sorghum tassels	0.95	0.82

From data obtained, the bulk density was decreased by the biochars added as soil bulk density without biochar was 1.20mg/mL. This is because of decreasing in soil compacting and increasing in water holding capacity. Bulk density is soil compacting therefore, those biochars in order to decrease this compaction; they increased spaces (porosity) between soil particles so, as a result this increases water infiltration and soil moisture which in turn favors plant roots to absorb adequate water needed for better growth hence fertility. However, biochars made in furnace decreased bulk density that biochars made in open environment; this because those biochars were made in different environment conditions for instance those made in high oxygen conditions contain low amount of aromatic carbon as a great amount of it was oxidized by oxygen.

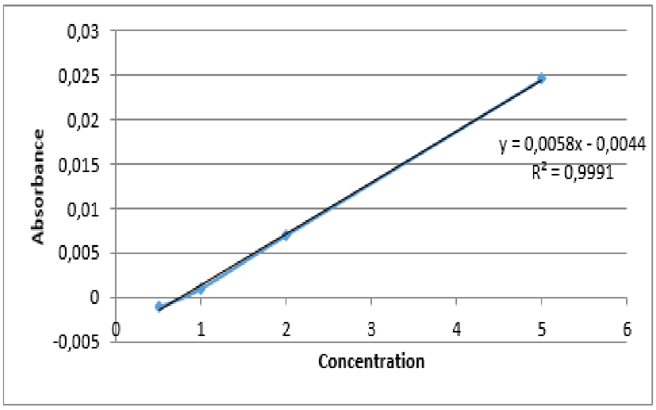
3.5. Heavy metals adsorption property of biochars in soil

First, standard solutions were prepared and external calibrations used to obtain the concentrations of heavy metals as follow.

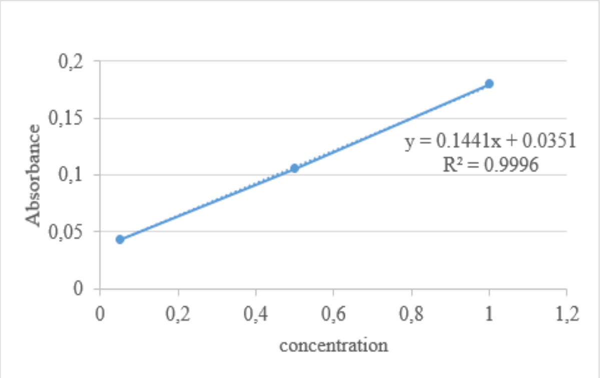
A standard plot of absorbance vs concentration for Cu



A standard plot of absorbance vs concentration for Mn



A standard plot of absorbance vs concentration for Cd



The external calibrations obtained were promising since R^2 was near to 1. Therefore this indicates that standard solutions were well prepared. However, external calibrations of Cu and Mn look like each other because there was data treatment for manganese in order to get limit of linearity where first two points were ignored. Generally, in this experiment heavy metals concentrations were measured in soil sample without biochars and after adding different biochars with soil they were also measured in order to see the changes on heavy metals concentrations. The results were recorded in the following table. The numbers 1 and 2 indicate biochars made in open environment and furnace respectively.

Table 6: *Results of heavy metals concentration in soil sample without biochar and biochar amended soil.*

Samples	Cu (mg/L)	Mn (mg/L)	Cd (mg/L)
Soil sample	0.1014	0.2050	-0.4947
Corn cobs1	0.0446	0.0115	-0.6128
Eucalyptus 1	0.0700	-0.0422	-0.1681
Potato peels1	0.0974	-0.0191	0.1557
Sorghum tassels1	-0.0494	-0.0639	0.1065
Corn cobs2	-0.1493	-0.0605	0.0005
Eucalyptus2	-0.2051	-0.0347	0.0343
Potato peels2	-0.2913	-0.0877	2.6325
Sorghum tassel2	-0.3040	-0.0883	0.1530

In general, for all metals, biochars have better sorption capacity than the original biomass, which can be explained by surface changes during the pyrolysis process, such as changes in porosity, functional groups and mineral content(J. J. Zhao et al., 2019). From data obtained, there was decrease in heavy metal concentrations in biochar amended soil compared to soil without biochar. Therefore, this is due to the high porosity and large surface areas of biochars which increase the adsorption efficiency of heavy metals. Moreover, from data obtained biochars made from furnace have decreased heavy metals in soil sample than biochars made in open environment. This is addressed to the factor that those biochars were made in different conditions and their differences in the mineral compositions such as K, Ca, Mg and P on their surface which are used for ion exchange with heavy metals. In addition, biochars from sorghum tassels have shown high adsorption compared to other biochars and biochars from corn cobs have shown low adsorption among biochars, this ranking can be attributed to the reason that biochars from sorghum tassels have high porosity and surface area with high mineral content than other biochars and biochars from corn cobs have low porosity, surface area and mineral content than other biochars. Lastly, from data obtained, there was no Cd in soil sample. However, in soil amended with biochars from potato peels and sorghum tassels; concentrations of Cd was observed and I recommend to study on concentrations of Cd in potato peels and sorghum tassels.

4. CONCLUSION AND RECOMMENDATION

Briefly, the physicochemical properties (PH, specific surface area, pore size, CEC, volatile mater, ash and carbon content) of biochar change with pyrolysis temperature and feedstock kind. Moreover, increasing temperature decreases the number of acidic functional groups, especially carboxylic functional groups, and causes the appearance of basic functional groups. This increase in basic functional groups is likely due to increase of ash content as temperature increases. Biochar has shown many advantages depending on its physicochemical properties for instance biochar can reduce soil acidity and increases soil electrical conductivity and cation exchange capacity (CEC), which results in higher nutrient availability to plants hence soil fertility, pollution remediation due to high CEC and specific surface area and carbon sequestration due to carbon and ash content. Additional benefits come from biochar's ability to adsorb contaminants, including inorganic and organic pollutants in the soil and leaching waters, thus improving soil and water quality. However, responses to biochars may depend on the type of biochar used and the specific characteristics of that biochar. Because biochar characteristics determine its suitability for specific agricultural or environmental purposes, biochar production must be made in such way to address such specific needs.Additionally, from our study , we recommend next researchers to study in deep on this other research in potato peels and sorghum tassels derived biochars.

REFERENCES

[1]. Glodowska, M., & Cultivation, P. (2017). Biochar characteristics and application in the agriculture. May.

[2]. Hunt, J., Duponte, M., Sato, D., & Kawabata, A. (2010). The Basics of Biochar : A Natural Soil Amendment 1. 1–6.

[3]. Joseph, S. Taylor, P. C. A. (2019). Basic Principles of Biochar Production - Biochar for Sustainable Soils. In Biochar for Sustainable Soils. https://www.e education.psu.edu/egee439/node/537%0Ahttps://biochar.international/guides/basic-principles-of-biochar-production/%0Ahttps://biochar.international/guides/basic-principles-of-biochar-production/#introduction

[4]. Juriga, M., & Šimanský, V. (2019). Effects of Biochar and its Reapplication on Soil pH and Sorption Properties of Silt Loam Haplic Luvisol. Acta Horticulturae et Regiotecturae, 22(2), 65–70. https://doi.org/10.2478/ahr-2019-0012

[5]. Li, X., Shen, Q., Zhang, D., Mei, X., Ran, W., Xu, Y., & Yu, G. (2013). Functional Groups Determine Biochar Properties (pH and EC) as Studied by Two-Dimensional 13C NMR Correlation Spectroscopy. PLoS ONE, 8(6). https://doi.org/10.1371/journal.pone.0065949

[6]. Mohammed, E., Mohammed, T., & Mohammed, A. (2017). MethodsX Optimization of an acid digestion procedure for the determination of Hg , As , Sb , Pb and Cd in fish muscle tissue. MethodsX, 4, 513–523. https://doi.org/10.1016/j.mex.2017.11.006

[7]. Singh, B., Dolk, M. M., Shen, Q., & Camps-Arbestain, M. (2017). Biochar pH, electrical conductivity and liming potential. Biochar: A Guide to Analytical Methods, June 2018, 23–38. https://ebooks.publish.csiro.au/content/ISBN/9781486305100

[8]. Tomczyk, A. (2020). Biochar physicochemical properties : pyrolysis temperature and feedstock kind effects. Reviews in Environmental Science and Bio/Technology, 3. https://doi.org/10.1007/s11157-020-09523-3

[9]. Wang, Yan; Liu, R. (2017). Comparison of characteristics of twenty-one types of biochar and their ability to remove multi-heavy metals and methylene blue in solution. 160.

[10]. Wang, S., Gao, B., Zimmerman, A. R., Li, Y., Ma, L., Harris, W. G., & Migliaccio, K. W. (2015). Physicochemical and sorptive properties of biochars derived from woody and herbaceous biomass. Chemosphere, 134, 257–262. https://doi.org/10.1016/J.CHEMOSPHERE.2015.04.062

[11]. Zhang, X., Wang, H., & He, L. (2013). Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. 8472–8483. https://doi.org/10.1007/s11356-013-1659-0

[12]. Zhao, J. J., Shen, X. J., Domene, X., Alcañiz, J. M., Liao, X., & Palet, C. (2019). Comparison of biochars derived from different types of feedstock and their potential for heavy metal removal in multiple-metal solutions. Scientific Reports, 9(1), 1–12. https://doi.org/10.1038/s41598-019-46234-4

[13]. Zhao, R., Coles, N., Kong, Z., & Wu, J. (2015). Effects of aged and fresh biochars on soil acidity under different incubation conditions. Soil and Tillage Research, 146(PB), 13–138. https://doi.org/10.1016/j.still.2014.10.014

Innocent IGIRANEZA received the degree of Bachelor of Science with honours in Chemistry, option of Environmental Chemistry at University of Rwanda, College of Science and Technology(UR/CST) in 2022. Since September 2022 I' am Biology and Chemistry trainer in secondary school.

Protogene Hakizimana received the Bachelor degree of Science in Applied Chemistry, option of Environmental Chemistry at University of Rwanda, College of Science and Technology(UR/CST) from 2011-2014 and Masters of Science in Environmental andDevelopment Studies, option of Environmental Economics and Natural Resource Management at University Of Lay of Adventists of Kigali (UNILAK)from 2016-2018. Since 2018 I am Assistant lecturer at University of Lay of Adventists of Kigali (UNILAK and from 2022 I am working at University of Rwanda / College of Medicine and Pharmacy.

Bayisenge Immaculee received a bachelor degree in Rural Development from 2007-2010 and student in Masters of environmental and Development studies at University of Lay Adventist of Kigali (UNILAK), Currently I am working at Trading Services Logistics , Rwanda.