African Journal of Agriculture and Food Science
ISSN: 2689-5331
Volume 6, Issue 1, 2023 (pp. 69-85)
www.abjournals.org

EFFECT OF PYROLYSIS TEMPERATURE ON CHEMICAL AND STRUCTURAL PROPERTIES OF RAW AGRICULTURAL WASTES

Azeez Musibau Oyeleke[1], Adesanwo Olusola Olajumoke[2],

Awoyefa Rofiyat[3] and Adediwura Joseph Oluwatosin[4]

[1]Department of Soil Science and Land Resources Management, Obafemi Awolowo University, Ile-Ife, Osun State, Nigeria. E-mail: mazeez@oauife.edu.ng

[2]Department of Soil Science and Land Resources Management, Obafemi Awolowo University, Ile-Ife, Osun State, Nigeria. E-mail: oadesanwo@oauife.edu.ng

[3]Department of Soil Science and Land Resources Management, Obafemi Awolowo University, Ile-Ife, Osun State, Nigeria. E-mail: jossydgold@gmail.com

[4]Department of Soil Science and Land Resources Management, Obafemi Awolowo University, Ile-Ife, Osun State, Nigeria. E-mail: jossydgold@gmail.com

Cite this article:

Azeez M.O., Adesanwo O.O., Awoyefa R., Adediwura J.O. (2023), Effect of Pyrolysis Temperature on Chemical and Structural Properties of Raw Agricultural Wastes. African Journal of Agriculture and Food Science 6(1), 69-85. DOI: 10.52589/AJAFS-YY75RSRK

Manuscript History

Received: 21 Feb 2023

Accepted: 9 April 2023

Published: 15 May 2023

ABSTRACT: *This study was carried out to assess the effect of charring on chemical and structural properties of raw agricultural wastes at two different temperatures. The agricultural wastes (feather from the poultry unit, maize cob, maize stalk, bamboo, rice straw, cocoa pods, maize husk and used paper from offices) were collected from Teaching and Research Farm, Obafemi Awolowo University (OAU), Ile-Ife, Osun State, Ife excluding the used paper, which was collected from the Academic areas, OAU. The collected waste materials were air-dried, pulverized, ground, and sieved with 2 mm sieve separately. Biochars were produced from raw agricultural wastes at pyrolysis temperatures 400℃ and 450℃. The raw and selected charred agricultural wastes were subjected to chemical and structural analyses. Pyrolysis of the raw materials at the two temperatures led to a significant increase in pH. A significant decrease in organic carbon of all the agricultural waste materials was observed after pyrolysis, a lower C:N was recorded; however, nitrogen content did not change significantly with pyrolysis temperature compared with the raw waste materials. The concentrations of cations like Ca and Mg were unaffected by the pyrolysis temperatures, but significant increase was observed with potassium. The results of FTIR analysis indicated the presence of many surface functional groups in both the raw and charred materials, such as OH, COOH and NH, that could be involved in adsorption and release of plant nutrients in soils, including heavy metals adsorption from soil. However, the intensities of the functional groups were lower in raw agricultural wastes compared with charred agricultural waste. The effect of temperature differences was not significant on the elemental and structural properties; thus, any could be taken as the optimum temperature for effective biochar production. It was concluded that biochar produced from agricultural wastes could be used as liming materials and soil amendments. Also, the presence of carboxylic and phenolic groups in the charred materials will increase the soil cation exchange capacity and improve the nutrient holding capacity of the soil.*

KEYWORDS: Pyrolysis, biochar, agricultural wastes, functional groups, nutrients, pH.

Article DOI: 10.52589/AJAFS-YY75RSRK
DOI URL: https://doi.org/10.52589/AJAFS-YY75RSRK

INTRODUCTION

A huge quantity of agricultural waste otherwise called agro-waste, consists of animal wastes (manure, animal carcasses), food processing waste, waste from cropping activities (corn stalks, sugarcane bagasse, drops, and culls from fruits and vegetables), are generated on a daily basis and poor management technique is a great threat to the well-being of the people and the environment in Nigeria. Most farmers embark on open burning of agricultural wastes. Although it helps in quick removal and destruction of pathogens, the negative effect is enormous. Many toxic gases such as carbon monoxide (CO), dioxins and furans, volatile organic compounds (VOC), carcinogenic polycyclic aromatic hydrocarbons (PAH), as well as fine inhalable particles are released into the atmosphere (Kim Oanh et al., 2011; Jenkins et al., 2003) as a result of open burning waste. There is likelihood of a significant increase in agricultural wastes globally due to intensification of farming activities for food production (Ashamo *et al.*, 2021).

Globally, it is estimated that about 998 million tonnes of agricultural wastes are produced yearly (Ratna *et al.*, 2022). Organic wastes can amount to as high as 80 percent of the total solid wastes generated in any farm of which manure production can amount up to 5.27 kg/day/1000 kg live weight, on a wet weight basis. The spiral increase in waste generation rate will lead to a rise in environmental challenges if not adequately managed (Johari *et al.*, 2012). These agricultural wastes are very rich in plant nutrients; therefore, a judicious method that will return them to the soil is highly desirable.

Production of biochar is gaining attention globally as a low cost and viable recycling method for solid wastes. Biochar is produced by thermochemical conversions, such as pyrolysis, gasification, hydrothermal process, and carbonization of carbonaceous biomass, such as agricultural residues, algal biomass, forest residues, manures, activated sludge, energy crops, etc. at high temperature (300℃- 900℃) under oxygen limiting conditions (Lehmann *et al.*, 2011). Its application can be used as a filter for tar reduction in pyrolysis and gasification, as fuel when pelletized, and used as a substrate to produce hydrogen (Paethanom *et al.*, 2012). Reports on the positive effects of biochar as a form of soil amendment, remediating organic or inorganic contaminants and mitigating greenhouse gas emission are well established and documented (Jeffery *et al.*, 2011; Novak *et al.*, 2016; Olubisi *et al.*, 2016; Yuan *et al.*, 2019). Although, the plant nutrient contents in biochar may be lower than the raw material, its effect on the nutrient holding capacity of the soil, climate change mitigation through carbon sequestration and chelation of organic pollutants make biochar a treasurable material for sustainable crop production and a good alternative to the open burning for soild waste management (Beesley *et al*., 2011). Scanty information is available on the percentage nutrient reduction in biochar produced, compared with raw agricultural waste in Nigeria.

Pyrolysis temperature affects the chemical and structural properties of biochar, such as pH, percent organic carbon and nitrogen, C:N ratio, basic cations, surface area, and functional groups (Tag *et al.*, 2016), and this can be related to the release of volatiles at high temperature (Sun *et al.*, 2014; Chatterjee *et al.*, 2020). Previous studies reported that high pyrolysis temperature led to increased biochar pH, percent carbon content but lower N content (Hossain *et al.*, 2011; Zhang *et al.*, 2017).

Article DOI: 10.52589/AJAFS-YY75RSRK
DOI URL: https://doi.org/10.52589/AJAFS-YY75RSRK

Therefore, the aim of this study was to assess the chemical and structural properties of raw agricultural wastes and the resultant biochar with a view to evaluate the effectiveness of biochar as a form of soil amendment.

MATERIAL AND METHODS

Sample Collection and Preparation

The agricultural wastes (feather, Myaize cob, maize stalk, bamboo, rice straw, cocoa pod, maize husk and paper) were collected from Teaching and Research Farm, OAU, Ile-Ife excluding the used paper, which was collected from the Academic areas, OAU. The wastes were air-dried, pulverized, and sieved with 2 mm sieve separately. Composite samples were taken from the bulk samples for chemical and structural analyses. The agricultural wastes were pyrolysed under two temperatures (400^0C and 450^0C) at Agronomy laboratory, University of Ibadan, Oyo State.

Laboratory Analysis

The pH of the raw and charred agricultural wastes was determined with a standardized digital pH meter in a 1:2 w/v suspension of the wastes and 0.01 M $CaCl_2$ after a 1-hour equilibration period, using the procedure outlined by Peech *et al*. (1965) with a review by Jindo *et al.* (2014). To determine the basic cations, 1 g of the raw and charred agricultural wastes was digested with 20 ml of concentrated H_2SO_4 for 2 hours and left overnight to cool completely. The digest was transferred into 50 ml volumetric flask, made up to mark with distilled water. The concentrations of Na and K were determined by a flame photometer while Ca, Mg were determined using atomic absorption spectrophotometer (AAS) (Zhang *et al*., 2002). Organic carbon was determined on 0.2 g sample using Walkley and Black (1934) method, while the total N was determined on 0.5 g sample using micro-Kjeldahl digestion and distillation procedure (Bremner & Mulvaney, 1982).

Structural Analysis

The raw and charred agricultural wastes were analyzed using Fourier Transform Infrared Spectroscopy (FTIR) in the range of 400 to 4000 cm^{-1} with Attenuated Total Reflectance (ATR) technique. A small amount of the sample was added to the mountain plate using a spatula to cover the exposed surface of the crystal, the pressure arm was placed on the top of the sample and then the nob was rotated until it touched the sample. The sample was scanned four times with the force gauge indicating a pressure of 100 and 130 pascal. The scanned result was printed and the mountain plate was cleaned with methanol to avoid contamination. The procedure was repeated for all the samples.

Statistical Analysis

The data obtained were analysed using R – statistical software version 3.6.0. (R core Team, 2019). The data were fitted by a generalized linear model with fixed effects representing different treatments. Post-hoc multiple pairwise comparisons were analysed by Tukey's significant differences using the CLD function implemented in the R package emmeans. For all analysis, the criterion used for statistical significance was $P < 0.05$.

Article DOI: 10.52589/AJAFS-YY75RSRK
DOI URL: https://doi.org/10.52589/AJAFS-YY75RSRK

RESULTS AND DISCUSSION

Chemical Composition of Raw Materials and Biochar

The results of pH, organic carbon (OC), total nitrogen and C:N ratios of the agricultural raw materials before and after pyrolysis at two temperatures (400^0C and 450^0C) are shown in Table 1. Generally, pyrolysis of the raw materials at the two temperatures led to significant increase in pH of all the agricultural raw materials used in this study. The biochar derived from cocoa pods at 400^0C and 450^0C had the highest pH (10.9 and 10.8 respectively) while the raw feather from poultry unit had the lowest pH value. This indicates that biochar from different waste materials could potentially serve as liming materials to remediate soil acidity similar to the previous study (Berek, 2014). The result of this study also indicated a direct positive effect of increasing pyrolysis temperature on pH; this was attributed to higher ash content and the presence of organic functional groups that contain oxygen (Zhao *et al*., 2017). Mechanisms controlling the increase in biochar pH involve the formation of carbonate and content of inorganic alkalis during pyrolysis resulting in alkaline condition. The organic carbon of different wastes decreases significantly after the pyrolysis process compared with raw waste materials, except feather, where steady increase in OC was observed at the two temperatures (Table 1). However, a previous study by Chun *et al*. (2004) also reported an increase in carbon content with increasing pyrolysis temperature, which was ascribed to the presence of certain amount of original organic plant residues, such as cellulose, in the produced biochar (Chun *et al*., 2004). The decrease in OC in the present study could be attributed to the conversion of organic carbon to inorganic carbon during the pyrolysis process. A gradual but not significant reduction was observed in the N content as the pyrolysis temperature increased; this is similar to a previous study (Chatterjee *et al*., 2020). Chatterjee *et al*. (2020) reported that percent total N content of the plant materials used in their study reduced by half after pyrolysis due to the volatilization of certain nutrients at a high temperature. The C:N ratios of most agricultural wastes decrease, except feather, which increases with pyrolysis temperature due to high organic carbon present in the raw materials. The lower C:N ratios of biochar is an indication of fast release of nutrients for plant uptake.

Table 1: Results of pH, organic carbon, total nitrogen, and C:N ratios of agricultural raw materials and resultant biochars at two different temperatures

Treatment	pH (0.01 M $CaCl_2$)			% Organic carbon			% Total nitrogen			C:N		
	Raw	400°C	450°C	Raw	400°C	450°C	Raw	400°C	450°C	Raw	400°C	450°C
Feather	3.7a	7.5de	9.1g	13.66gh	20.65i	17.97hj	0.29b	0.05a	0.04a	47	413	449
Maize cob	7.8ef	10.1h	10.2hi	6.99f	2.13a	2.13a	0.05a	0.08a	0.06a	139	27	36
Maize stalk	8.2f	10.1h	10.6ij	16.95h	3.13cd	3.13cd	0.31b	0.04a	0.03a	55	78	104
Bamboo	5.4b	10.2h	10.1hi	11.79g	4.68e	7.03f	0.27b	0.92b	0.04a	44	5	176
Rice straw	5.9c	8.1f	7.9ef	23.01j	2.93bc	3.32cd	0.04a	0.05a	0.04a	575	59	83
Cocoa pod	8.9g	10.9j	10.8j	16.97h	2.34a	3.12cd	0.08a	0.04a	0.05a	212	59	62
Maize husk	5.4b	10.4i	9.8h	30.62k	2.73a	4.10de	0.14a	0.09a	0.09a	219	30	46
Paper	7.3d	9.1g	9.7h	31.2k	3.12cd	2.15a	0.42b	0.24b	0.14a	74	13	15

The comparison was done for raw biochar at 400°C and 450°C for each chemical parameter; different letters in the same column indicate a statistically significant difference among the treatments at a 5% significance level.

Table 2: Results of basic cations in raw agricultural wastes and resultant biochars at two different temperatures

Treatment	Calcium (cmolkg^{-1})			Magnessium (cmolkg^{-1})			Potassium (cmolkg^{-1})		
	Raw	400°C	450°C	Raw	400°C	450°C	Raw	400°C	450°C
Feather	0.01a	0.03a	0.03a	0.02a	0.04a	0.04a	0.33b	0.67b	8.0ef
Maize cob	0.02a	0.02a	0.01a	0.08a	0.03a	0.06a	1.55c	2.59d	2.51d
Maize stalk	0.02a	0.01a	0.01a	0.05a	0.01a	0.02a	3.62d	13.36f	8.7ef
Bamboo	0.09a	0.02a	0.08a	0.07a	0.06a	0.06a	1.76c	3.7d	4.62d
Rice straw	0.01a	0.01a	0.02a	0.07a	0.05a	0.06a	0.94b	1.61c	1.67c
Cocoa pod	0.08a	0.05a	0.04a	0.08a	0.06a	0.08a	5.82e	11.05f	10.70k
Maize husk	0.01a	0.02a	0.02a	0.05a	0.04a	0.06a	1.4c	6.21e	6.76e
Paper	0.04a	0.23b	0.05a	0.02a	0.07a	0.21b	0.05a	0.34b	0.20ab

The comparison was done for raw biochar at 400°C and 450°C for each chemical parameter; different letters in the same column indicate a statistically significant difference among the treatments at a 5% significance level.

The results of basic cations in the raw materials and resultant biochar (400^0C and 450^0C) are presented in Table 2. The effect of pyrolysis temperature was not significant on calcium and magnesium contents of the produced biochar. However, the pyrolysis temperature of 400^0C and 450^0C significantly increased the potassium contents of the biochar. The increase could be ascribed to the increase in the ash contents of biochar samples (Zhou *et al.,* 2013).

Results of FTIR Analysis

Raw and pyrolyzed agricultural wastes at 400^0C (cocoa pod, maize husk, paper, rice straw, feather, maize stalk, maize cob and bamboo) were subjected to Fourier Transformed Infra-red Spectroscopic (FTIR) analysis to identify the functional groups that dominate the exchange sites (Figures 1-8a and 1-8b). The biochars produced at 400^0C were selected because no significant effect of the varying temperatures was oberserved on the elemental composition of both biochar materials. The figures revealed FTIR spectrum of the typical functional group at wavenumber of 2000-4000 cm^{-1} and fingerprint from 500-1500cm^{-1}. The most common important features are broad band at 3000-3902 cm^{-1} associated with OH stretch of OH groups, peak at 2900-2955 cm^{-1} due to aliphatic C-H stretching, peak at 2500 cm^{-1} due to OH stretch from strongly H-bonded –COOH, strong peak at 1640-1700 cm^{-1} associated to structural vibrations of aromatic C=C, anti symmetric stretching of COO groups and 900-1100 cm^{-1} C-O stretching and OH bending of alcoholic and phenolic OH and COO asymmetric stretch. In addition, other functional groups detected in biochar samples include N-H bend, C-O-O stretch, methyl group, aromatic phosphates and cyclo-alkanes (Manikandan & Subramanian, 2015; Janu *et al.* 2021). There is the presence of Si-O-Si bond in rice straw biochar because Si is the main structure and it continues to be present at high temperature during pyrolysis. The presence of higher functional groups in biochar, particularly in maize cob, than raw samples, suggest that if biochar produced from different agricultural wastes are applied as soil amendments, it will increase soil cation exchange capacity with consequent higher nutrient release for plant uptake.

Article DOI: 10.52589/AJAFS-YY75RSRK
DOI URL: https://doi.org/10.52589/AJAFS-YY75RSRK

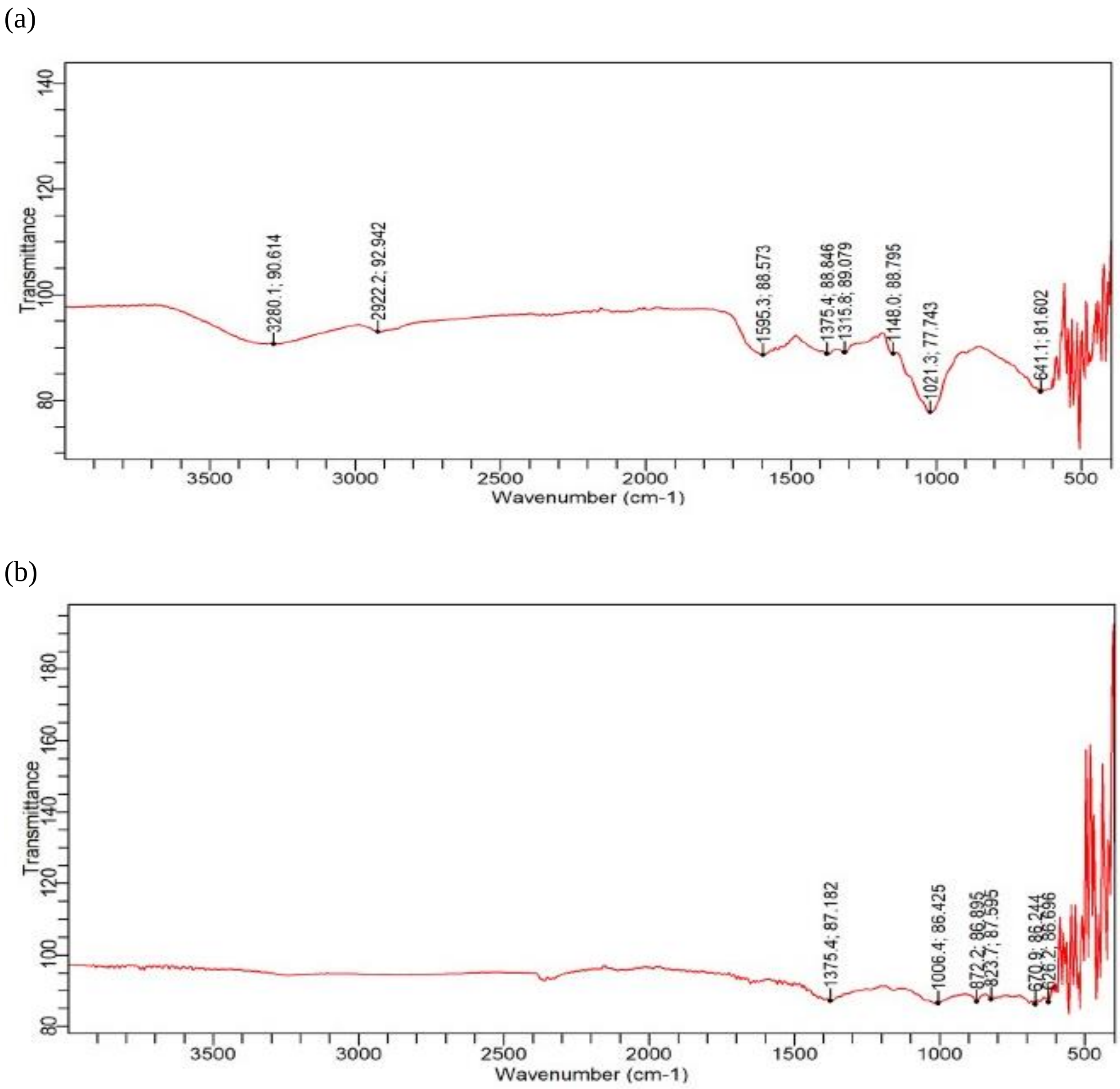


Figure 1: The structural properties of cocoa pod before (a) and after (b) pyrolysis at 400^0C

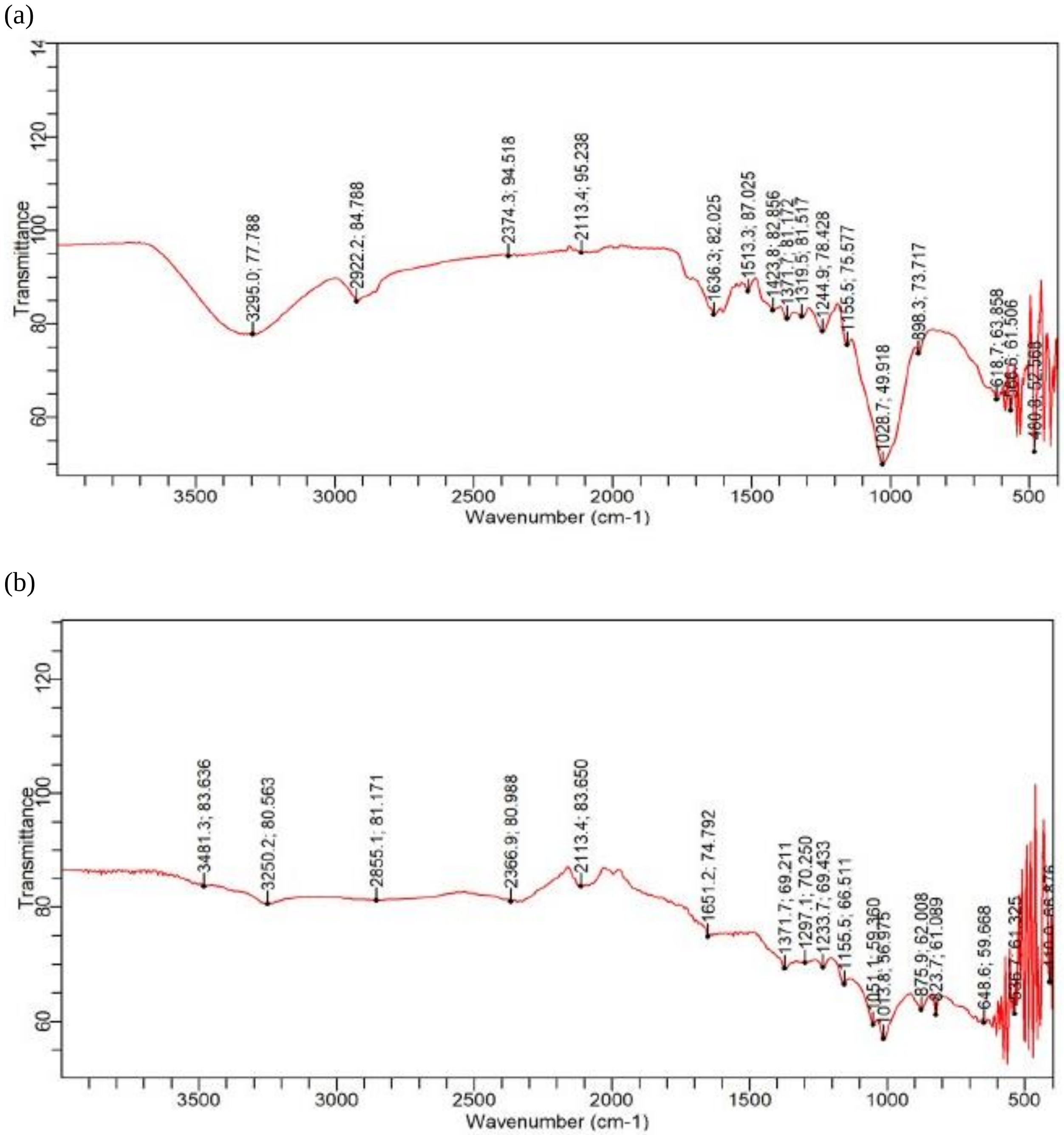


Figure 2: The structural properties of maize husk before (a) and after (b) pyrolysis at 400^{0}C

Article DOI: 10.52589/AJAFS-YY75RSRK
DOI URL: https://doi.org/10.52589/AJAFS-YY75RSRK

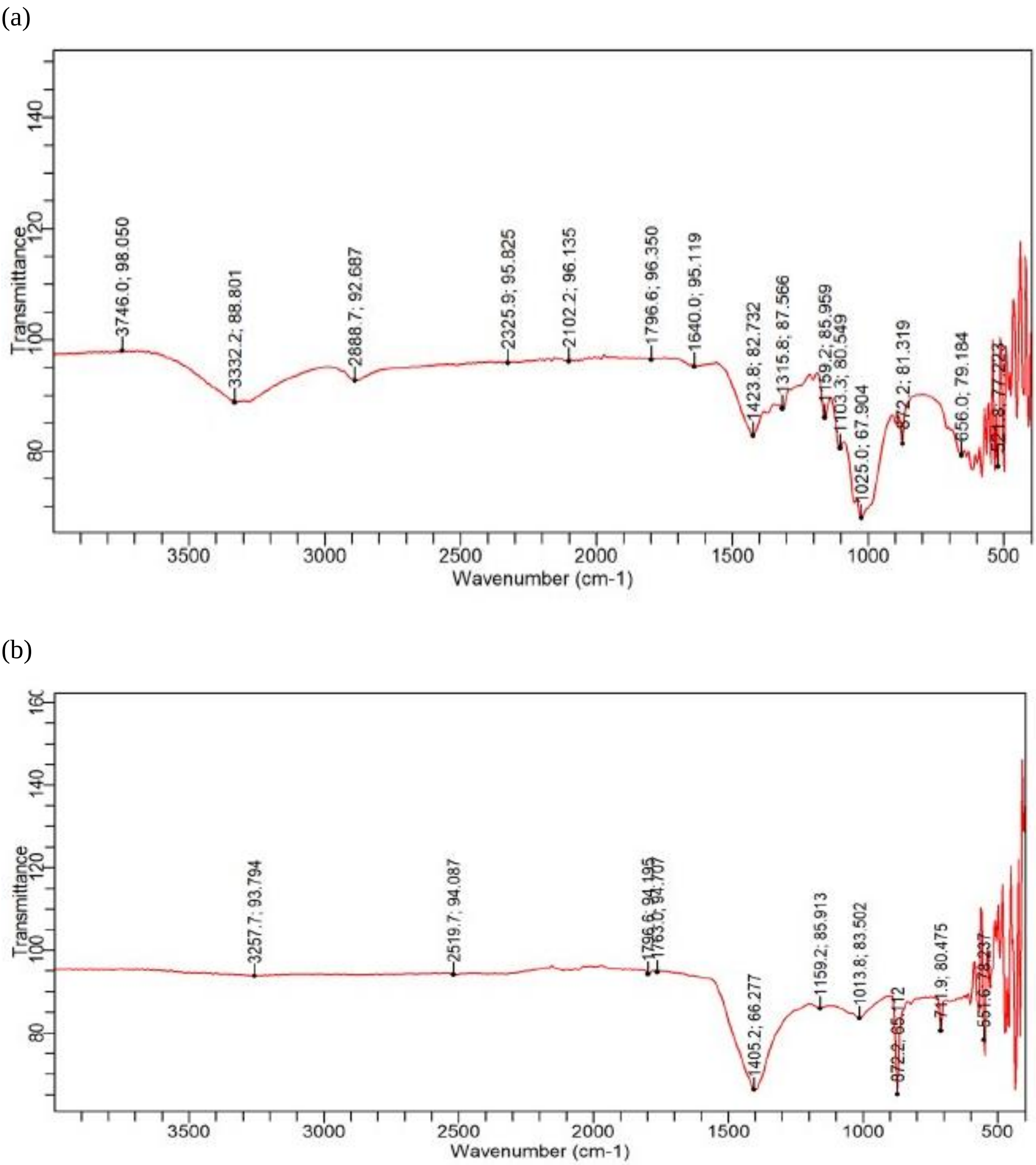


Figure 3: The structural properties of paper before (a) and after (b) pyrolysis at 400^0C

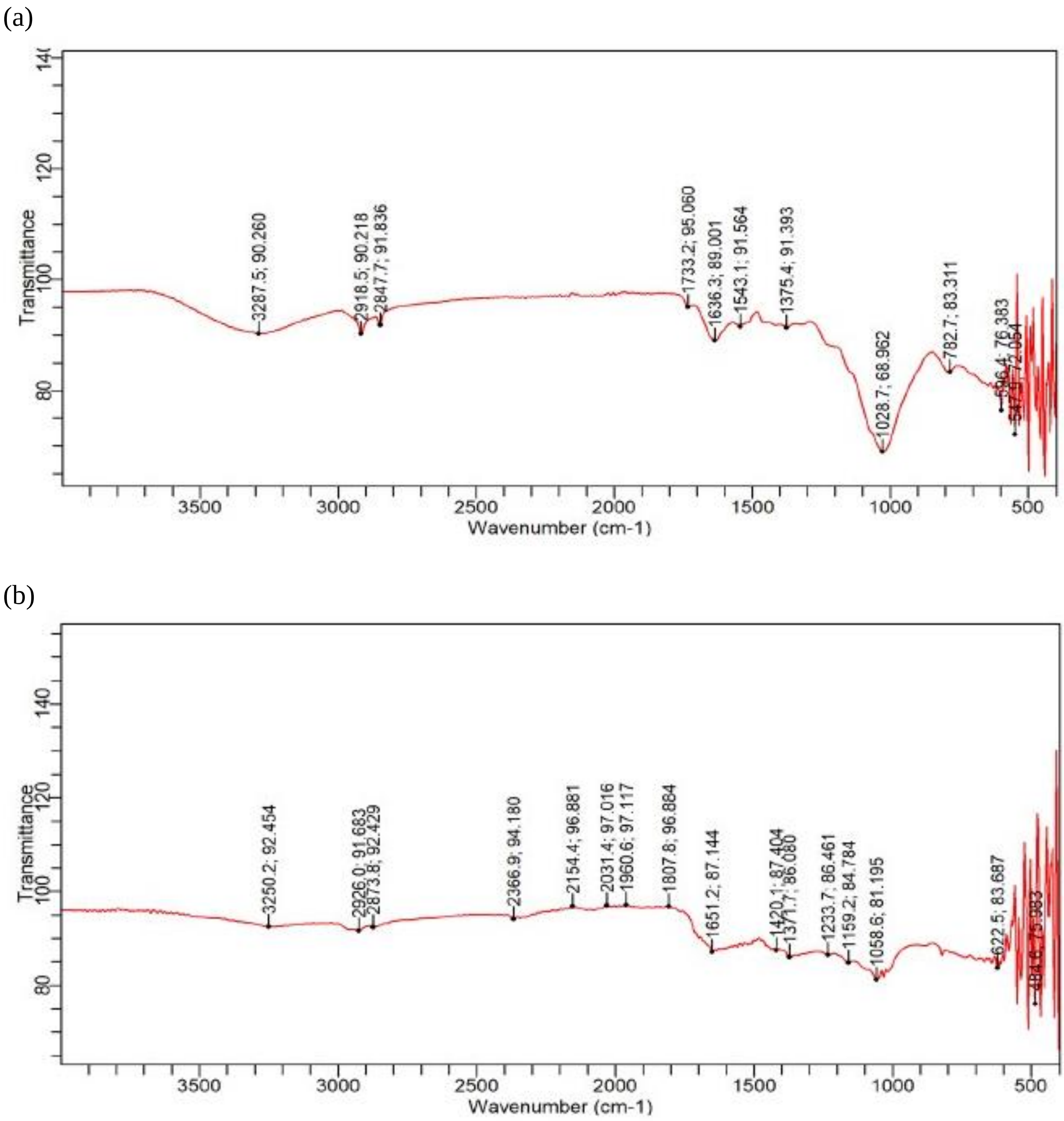


Figure 4: The structural properties of rice straw before (a) and after (b) pyrolysis at 400^0C

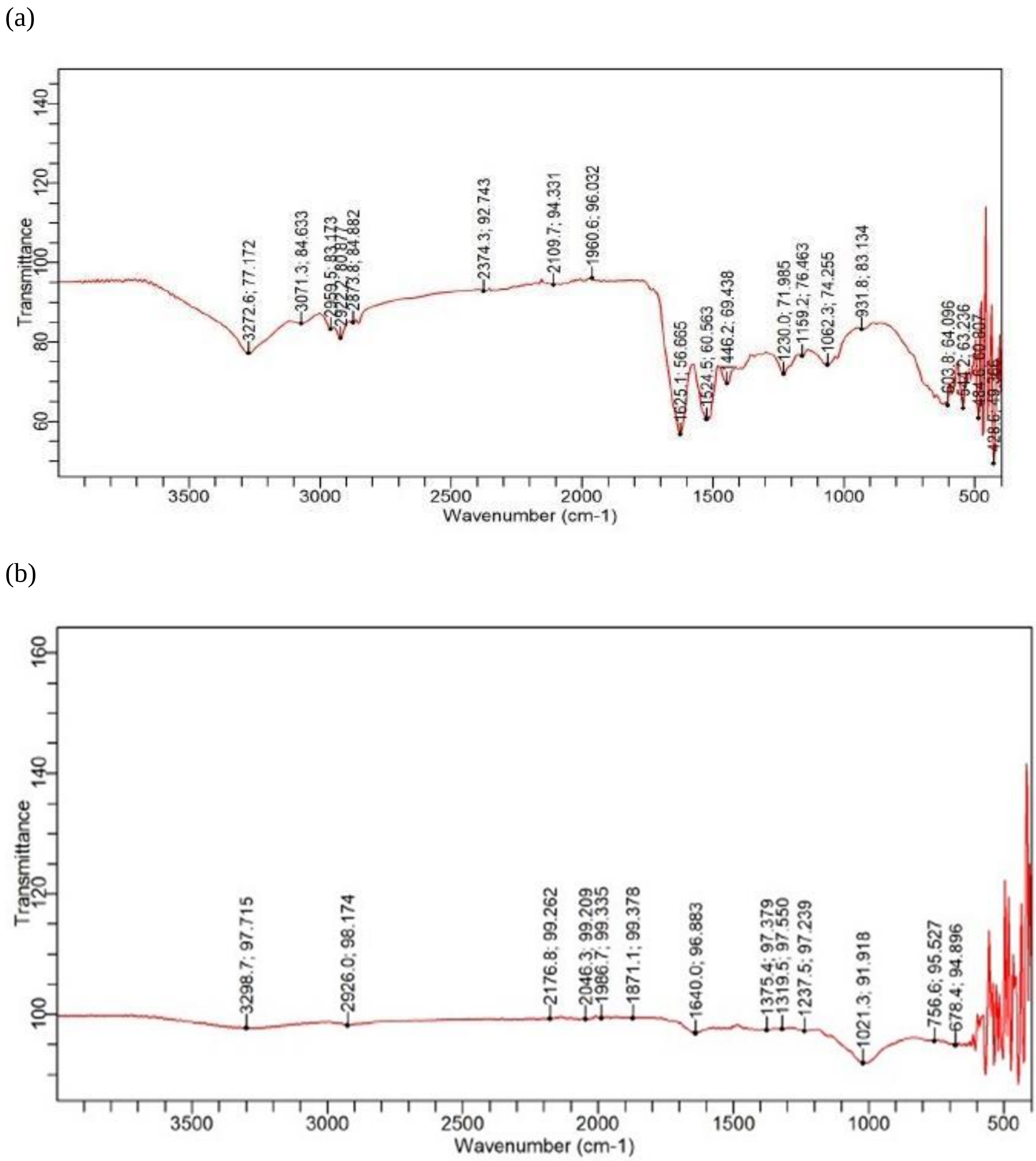
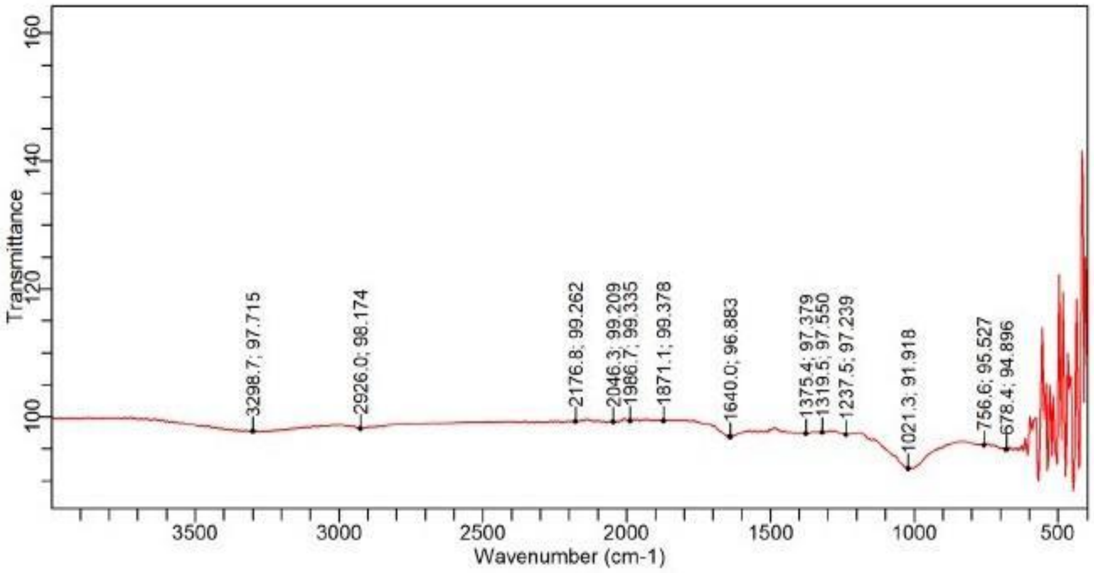


Figure 5: Structural composition of feather before (a) and after (b) pyrolyses

(a)



(b)

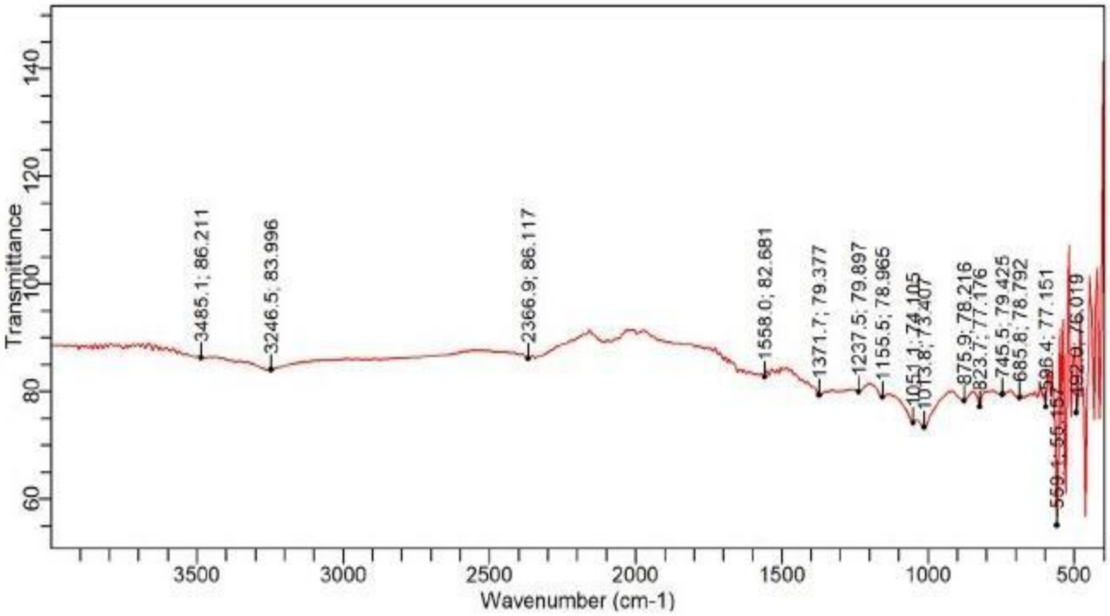


Figure 6: Structural composition of maize stalk before (a) and after (b) pyrolysis

(a)

Article DOI: 10.52589/AJAFS-YY75RSRK
DOI URL: https://doi.org/10.52589/AJAFS-YY75RSRK

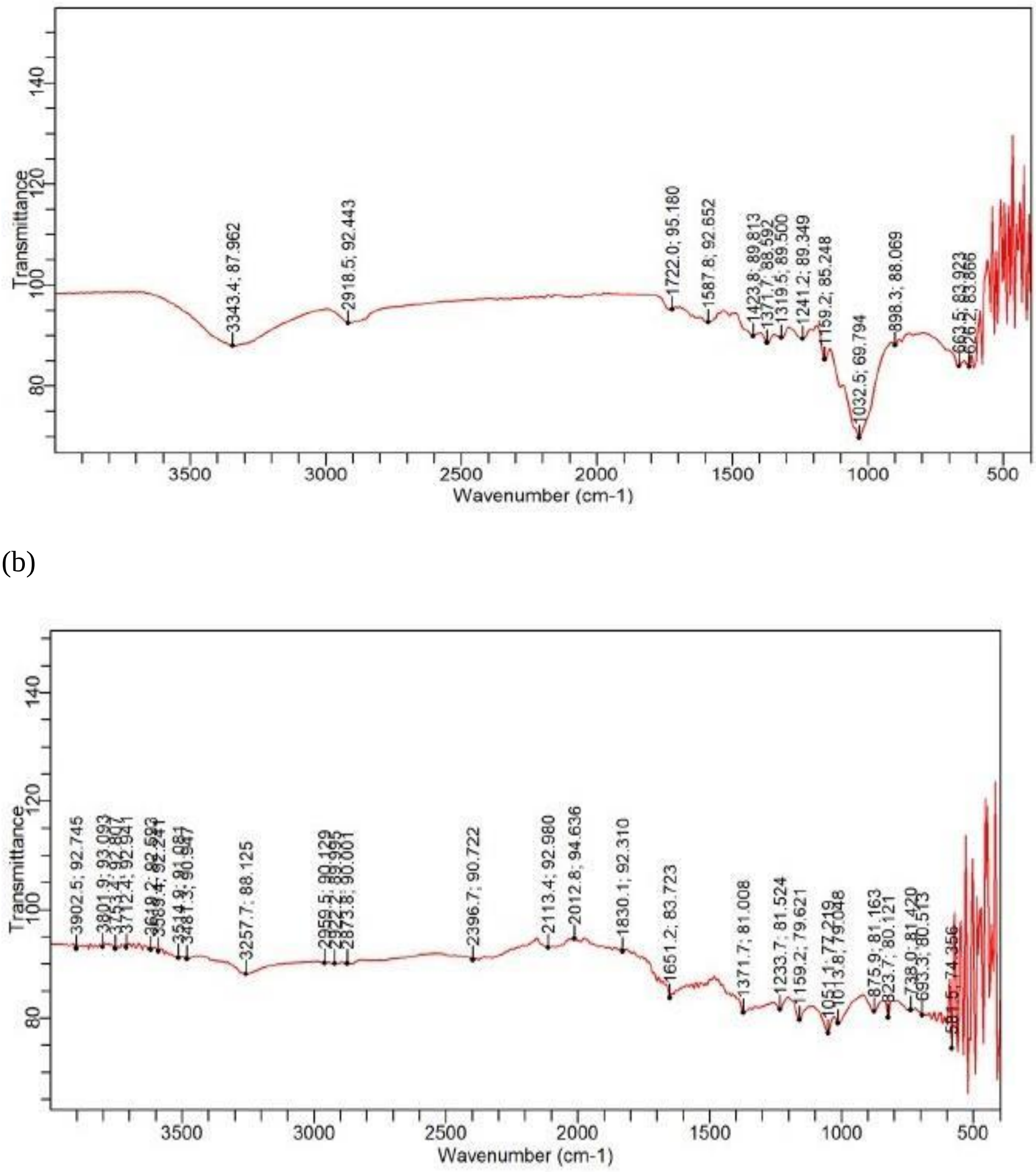


Figure 7: Structural composition of maize cob before (a) and after (b) pyrolyses

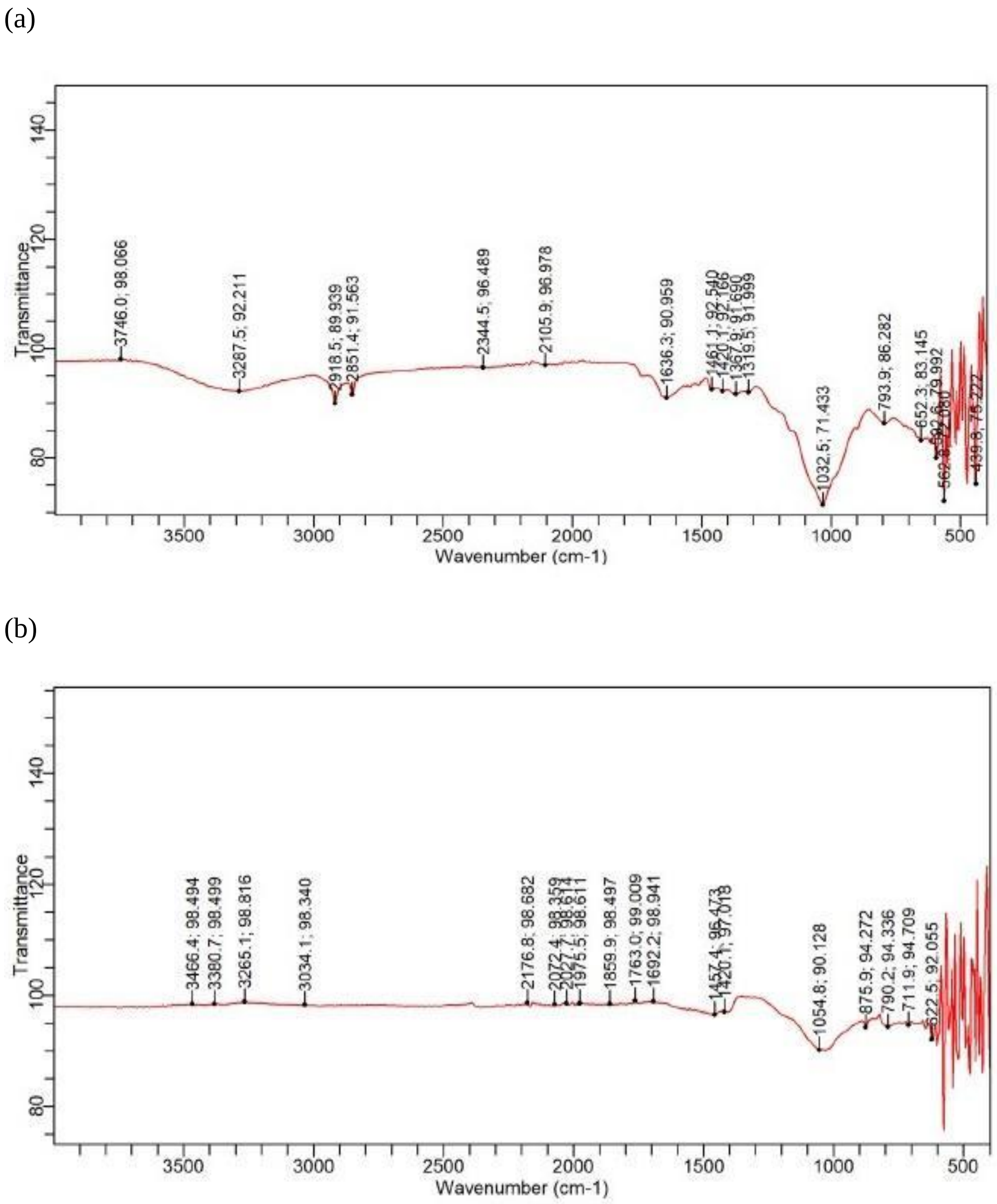


Figure 8: Structural composition of bamboo before (a) and after (b) pyrolysis

CONCLUSION

This study was conducted to assess the effect of charring on chemical and structural properties of raw agricultural wastes under two different temperatures (400^0C and 450^0C). Despite the increase in pH and potassium contents of the produced biochar, the percent organic carbon was significantly lower when compared with raw agricultural wastes and this was attributed to the conversion of organic carbon to inorganic carbon during pyrolysis process, whereas other chemical properties did not significantly change during pyrolysis, suggesting that biomass composition and temperature are key factors in biochar production. The pyrolysis temperatures used in this study influenced the measured parameters of the produced biochar in a similar way, indicating that both temperatures were optimum for effective biochar production. The produced biochars can be used to ameliorate soil acidity. The FTIR results indicated the capacity of the biochars to enhance the nutrient holding capacity of the soil. Further study on the field is highly recommended to demonstrate the performance of biochar under different temperatures on nutrient uptake by plants.

REFERENCES

Ashamo, M.O., Ileke, K.D. & Onasile, A.I. (2021). Chemical composition and toxicity of some Agro waste-derived insecticides against Angoumois grain moth, *Sitotroga ceralella* (Olivier) [Lepidoptera: Gelechiidae] infesting stored paddy grains. *Bulletin of the National Research Cent*re, 45 (25), 1-12 . https://doi.org/10.1186/s42269-020-00473- y.

Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J. L., Harris, E., Robinson, B. & Sizmur, T. A. (2011). A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. *Environmental Pollution*159(12):3269-3282. doi: 10.1016/j.envpol.2011.07.023.

Berek, A. K. (2014). Exploring the potential roles of biochars on land degradation mitigation. *Journal of degraded and mining lands management*, 1(3), 149-158.

Bremner, J. M. & Mulvaney, C. S. (1982). Nitrogen-total, In: Methods of Soil Analysis. Part 3. Chemical Methods, Vol. 5 of Soil Science Society of America Book Series, Ed. BySarks D.L. *Soil Science Society of America./ American Society of Agronomy*. Madison, WI 1085-1112.

Chatterjee, R., Sajjadi, B., Chen, W., Mattern, D. L., Hammer, N., Raman, V., & Dorris, A. (2020). Effect of Pyrolysis Temperature on PhysicoChemical Properties and Acoustic-Based Amination of Biochar for Efficient CO2 Adsorption. *Frontiers in Energy Research*, 8(85), 1-18 https://doi.org/10.3389/fenrg.2020.00085.

Chun, Y., Sheng, G. Y., Chiou, C. T. & Xing, B. S. (2004). Compositions and sorptive properties of crop residue-derived chars. *Environmental Science and Technology*, 38, 4649–4655.

Hossain, M. K., Strezov, V., Chan, K. Y., Ziolkowski, A. &Nelson, P. F. (2011). Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. *Journal of Environmental Management*, 92, 223–228. doi: 10.1016/j.jenvman.2010.09.008.

Janu, R., Mrlik, V., Ribitsch, D., Hofman, J., Sedláček, P., Bielská, L., & Soja, G. (2021). Biochar surface functional groups as affected by biomass feedstock, biochar composition and pyrolysis temperature. Carbon Resources Conversion, 4, 36-46. https://doi.org/10.1016/j.crcon.2021.01.003

Jeffery, S., Verheijen, F. G. A., van der Velde, M. & Bastos, A. C. (2011). A Quantitative Review of the Effects of Biochar Application to Soils on Crop Productivity Using Meta-Analysis. *Agriculture, Ecosystem and Environment*,144,175–187. doi:10.1016/j.agee.2011.08.015

Jenkins, J.C, Chojnacky, D.C, Heath, L.S. & Birdsey, R.A. (2003). National-scale biomass estimators for United States tree species. *Forest Science*, 49, 12-35.

Jindo, K., Matsumoto, K., García Izquierdo, C., Sonoki, T. & Sanchez-Monedero, M. A. (2014). Methodological interference of biochar in the determination of extracellular enzyme activities in composting samples, *Solid Earth*, 5, 713–719, https://doi.org/10.5194/se-5- 713-2014, 2014.

Johari, A., Hashim, H., Mat, R., Alias,H., Hasshim, M.H.& Rozainee M. (2012). Generalization, formulation and heat contents of simulated msw with moisture content. *Journal of Engineering Science and Technology*, 7 (6), 701-710.

Kim Oanh, N. T., Bich, T. L., Tipayarom, D., Manadhar, B. R., Prapat, P., Simpson, C. D. & Liu, J. S. (2011). Characterization of Particulate Matter Emission From Open Burning of Rice Straw. *Atmospheric Environment*, 45(2), 493-502. https://doi.org/10.1016/j.atmosenv.2010.09.023

Lehmann, J., Rillig, M. C., Thies, J., Masiello, C. A., Hockaday, W. C., & Crowley, D. (2011). Biochar effects on soil biota – A review. *Soil Biology and Biochemistry*, 43(9), 1812-1836. https://doi.org/10.1016/j.soilbio.2011.04.022.

Manikandan, A. & Subramanian, K.S. (2015). Ability of Urea Impregnated biochar fertilizers for securing the slow release of Nitrogen in Soils-Preliminary study. *International Journal of Agriculture Sciences*. 7 (11): 750-756.

Novak, J., Sigua, G., Watts, D., Cantrell, K., Shumaker, P., Szogi, A., Johnson, M. G., & Spokas, K. (2016). Biochars impact on water infiltration and water quality through a compacted sub-soil layer. *Chemosphere*, 142,160-167. https://doi.org/10.1016/j.chemosphere.2015.06.038.

Olubisi, O. J, Adesanwo, O.O., Fagbenro, J. A, Azeez, M. O. & Olufemi, T. A. (2016). Fourier Transform Infrared Spectroscopy Analysis of Urea Intercalated Biochar. *Proceedings of the 2nd Annual Conference of Biochar Initiative of Nigeria, 6-9 September 2016, Bowen University, Iwo, Osun state Nigeria*, 5-10.

Paethanom, A. & Kunio, Y. (2012). "Influence of Pyrolysis Temperature on Rice Husk Char Characteristics and Its Tar Adsorption Capability". *Energies*, 5 (12), 4941-4951. https://doi.org/10.3390/en5124941.

Peech, M. (1965). Methods of Soil Analysis: Part 2 Chemical and Microbiological Properties, Properties, 9:159-165, Second Edition. Agronomy Monographs.

Ratna, A. S., Ghosh, A., & Mukhopadhyay, S. (2022). Advances and prospects of corn husk as a sustainable material in composites and other technical applications. *Journal of Cleaner Production*, *371*, 133563. https://doi.org/10.1016/j.jclepro.2022.133563

R Core Team (2019). A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria, In., 275-286.

Sun, Y., Gao, B., Yao, Y., Fang, J., Zhang, M., Zhou, Y., Chen, H. & Yung L. (2014). Effects of feedstock type, production method, and pyrolysis temperature on biochar and hydrochar properties. *Chemical Engineering Journal*, 240, 574–578. doi: 10.1016/j.cej.2013.10.081

Tag, A. T., Duman, G., Ucar, S. & Yanik, J. (2016). Effects of feedstock type and pyrolysis temperature on potential applications of biochar. *Journal of Analytical and Applied Pyrolysis*, 120, 200–206. doi: 10.1016/j.jaap.2016.05.006.

Walkley, A. & Black, C. A. (1934). An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Science*, 37, 27-38.

Yuan, P., Wang, J., Pan, Y., Shen, B., & Wu, C. (2019). Review of biochar for the management of contaminated soil: Preparation, application and prospect. *Science of The Total Environment*, 659, 473-490. https://doi.org/10.1016/j.scitotenv.2018.12.400

Zhang, F.-S., Yamasaki, S., and Nanzyo, M. (2002). Waste ashes for use in agricultural production: I. Liming effect, contents of plant nutrients and chemical characteristics of some metals. Science of The Total Environment, 284(1-3), 215–225. doi:10.1016/s0048-9697(01)00887-7.

Zhang, H., Chen, C., Gray, E. M. & Boyd, S. E. (2017). Effect of feedstock and pyrolysis temperature on properties of biochar governing end use efficacy. *Biomass Bioenergy*, 105, 136–146. doi: 10.1016/j.biombioe.2017. 06.024.

Zhao, L., Zheng, W., Mašek, O., Chen, X., Gu, B., Sharma, B. K., & Cao, X. (2017). Roles of Phosphoric Acid in Biochar Formation: Synchronously Improving Carbon Retention and Sorption Capacity. *Journal of Environment Quality*, 46(2), 393. doi:10.2134/jeq2016.09.0344.

Zhou, Y., Gao, B., Zimmerman, A. R., Fang, J., Sun, Y., & Cao, X. (2013). Sorption of heavy metals on chitosan-modified biochars and its biological effects. *Chemical Engineering Journal*, 231, 512–518. doi: 10.1016/j.cej.2013.07.03.