Biological Forum – An International Journal **15(9): 887-892(2023)**

ISSN No. (Print): 0975-1130
ISSN No. (Online): 2249-3239

Novel Green Approach for the Synthesis of Nano biochar using Plant Resources and Botanical Extracts

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(Received: 06 July 2023; Revised: 04 August 2023; Accepted: 05 September 2023; Published: 15 September 2023)
(Published by Research Trend)

ABSTRACT: This experiment was carried out in 2021-2022 to synthesize nano biochar using Mint (*Mentha piperita*) and Nettle Extract (*Urtica diocia*). Three different biochar materials (Apple twig, Maize stalk and Walnut shell) were subjected to pyrolysis at 400°C for 1 hour. Green synthesis methods, employing plant extracts, were employed as eco-friendly alternatives to physical and chemical methods. Characterization of the synthesized nano biochars was conducted using SEM (Scanning electron microscopy), XRD (X-ray powder diffraction), and FT-IR (Fourier transform infra-red spectroscopy). SEM analysis revealed that nano biochars produced from Mint extract had average sizes of 50.0 nm to 148.0 nm, 68.0 nm to 112.0 nm, 70.0 to 155.0 nm with average size 85.8 nm, 92.4 nm and 105.2 nm for Apple twig, Maize stalk, and Walnut shell nano biochars, respectively. While those synthesized from nettle extract had average sizes of 78.0 to 120.0 nm, 50.0 to 100.0 nm and 50.0 to 140.0 nm with an average size of 97.8, 81.6 and 95.0 nm. These nano biochars exhibited various shapes, including spherical, cylindrical, plate-like, and flattened, as confirmed by SEM analysis. XRD analysis established their crystalline nature. FTIR study indicated alterations in functional groups among all biochars, highlighting the impact of plant extracts on their composition and properties. This work offers a quick, simple and non-toxic method for the synthesis of nano biochar.

Keywords: Nano biochar, Green synthesis, Plant extracts, Pyrolytic temperature, SEM, XRD, FT-IR.

INTRODUCTION

The word "biochar" is a combination of "bio" (from "biomass") and "char" (from "charcoal") and was first adopted in 1998 but extensively used from 2006. Biochar, a black, porous, and carbon-rich material, is produced through the pyrolysis of biomass in oxygen-deprived conditions at temperatures of 350-600°C (Guizani *et al.*, 2016). Its versatile applications can be grouped into four key areas. Firstly, it aids in climate change mitigation by locking carbon away in the soil for extended periods. Secondly, biochar contributes to energy production through pyrolysis, harnessing renewable energy sources. Thirdly, it enhances soil quality and fertility, promoting healthier plant growth and sustainable agriculture. Lastly, biochar serves as an effective waste management solution, converting biomass residues into a valuable resource. Overall, biochar stands as a multifaceted tool addressing climate change, energy needs, soil health, and waste reduction (Verma *et al.*, 2012: Lehmann and Joseph 2009). Bulk biochars (0.04- 20 mm) are widely utilized for agronomic and environmental purposes. Several research have recently shown the breakdown of bulk biochars into nanoscale particles (Spokas *et al.*, 2014). In comparison with bulk biochars, nano biochar with a size of 100 nm has been shown to have exceptional mobility in soils and can even be transported into groundwater (Chen *et al.*, 2017). In contrast to the promising benefits of bulk biochar, such as retention of nutrients and immobilizing potentially hazardous substances, nano biochar as a carrier could accelerate the migration of natural solutes and pollutants (Lian and Xing 2017). Metallic nanoparticle manufacturing is a topic of debate in nanoscale application research. A range of chemical and physical processes have been documented for the synthesis of metallic nanoparticles (Prakash *et al.*, 2009), including chemical reduction, electrochemical reduction (Zhang, 2008), chemical vapour deposition (Coulombe *et al.*, 2007), thermal breakdown (Kim *et al.*, 2006), and solvo thermal reduction (Tang *et al*., 2006). The aforementioned methods, on the contrary, have a number of disadvantages, such as the use of chemicals which are toxic, the generation of hazardous by products & significant energy consumption. As a result, there is an increasing need to create clean, dependable, biocompatible, cost-effective, and eco-friendly procedures for nanoparticulate material manufacturing. Biological means of synthesis is a superior substitute that does not use toxic chemicals, which is encouraging further researchers to consider biological systems as potential eco-friendly nano-factories. Trying to exploit nature's diversity of biological resources is a potential technique for obtaining high yield through low-cost, environmentally sustainable and sustainable nanoparticle production procedures. Biological techniques that utilize plant leaf extracts have been proposed as promising environmentally friendly alternative to chemical and physical processes for the production of low-cost, energy-efficient, and non-toxic metallic nanoparticles (Narayanan and Sakthivel 2010; IIliger *et al.,* 2021) because it bypasses the time-consuming procedure to sustain cell culture, the utilization of plant-based extracts for manufacturing of nanoparticle may be more effective to other ecologically friendly biological techniques (Talib *et al*., 1998). Another benefit of utilizing plants for nanoparticle synthesis is that they are widely available, safe to handle and containing a diverse range of phytochemicals that aid in the lowering process. Plant extracts are currently being used for biosynthesis of metal nano-particles. *Azadirachta indica* (Neem) (Shankar *et al*., 2004), *Emblica officinalis* (Amla) (Amkamwar *et al*., 2005), Mangosteen leaf and *Chenopodium album* Dhanaraj (2011) have all been described as having medicinal benefits. Biomolecules such as proteins, phenols and flavonoids have been shown in studies to have a vital role in not only decreasing ions to nano-size, but also in capping nanoparticles.

MATERIALS AND METHODS

This experiment on Synthesis, Standardization and Characterization of Nanobiochar was carried out during 2021 and 2022 at Sher-e-Kashmir University of Agricultural Sciences and Technology of Kashmir, Faculty of Horticulture, Division of Soil Science. For synthesis of Nano biochar 100 ml of distilled water was added to 10 g of dried mint and nettle leaf powder. After that, heat the material at 60°C for an hour. The content was then filtered using Wattman filter paper 40 and centrifuged for 15 minutes at 4000 rpm. After that, the plant extract was autoclaved and stored at 4°C for future research (Awwad *et al*., 2015; Kulkarni *et al*., 2015; Illiger *et al*., 2021). After that take 5 grams of each biochar (Apple twigs, Maize stalks, and Walnut shells) and add 100 ml of distilled water and 10 ml of above leaf extracts in each biochar separately. The contents were then be centrifuged at 4000 rpm for 15 minutes before being heated at 60°C for a period of two hours. The solid portion was shade dried after centrifugation and the supernatant solution was discarded. Then these synthesized nanobiochars were characterized by various techniques which were carried out at National Institute of Technology (NIT) Srinagar, Kashmir. XRD: An X-ray diffractometer was used to record the XRD examination of nano-materials. Smart Lab X-ray Diffractometer machine was employed for X-ray diffraction studies. In X-ray diffraction examinations, both phase variety and particle size were determined using a scanning range of 10-70 and a bond angle of 2. The specimen of powder was collected for XRD analysis and then placed on a glass slide for examination. SEM: The morphology (size and shape) of nanobiochars was studied using a Gemini SEM500 equipment in this investigation. A small amount of nano biochar powder was placed on a carbon coated copper grid before being transferred to a microscope operating at a 20kV accelerated voltage. Image J software was used to capture and analyze the acquired SEM images. FT-IR: After oven drying the biochar samples were mixed with spectroscopic grade KBr in the ratio of 100:1. Then the biochar mixed with KBr was compressed by hydraulic mill until the mixture became pellets. FTIR-ATR (Make–Agilent technologies) was used to obtain spectra. The spectra were obtained between 4000 and 500cm^{-1} at the resolution of 2 cm^{-1} resolution. Then Origin software was used for analyzing data and for interactive graphing.

RESULTS AND DISCUSSION

The surface morphology of nanobiochars were observed by SEM spectra (Fig. 1). The size of Apple twigs, Maize stalk and Walnut shell nano biochar synthesized from mint and analyzed by SEM ranged from 50.0 nm to 148.0 nm, 68.0 nm to 112.0 nm, 70.0 to 155.0 nm with average size of 105.2 nm with average size 85.8 nm, 92.4 nm and 105.2 nm. While the size of above mentioned nanobiochars synthesized from nettle as revealed by SEM ranged from 78.0 to 120.0 nm, 50.0 to 100.0 nm and 50.0 to 140.0 nm with an average size of 97.8, 81.6 and 95.0 nm. The shape of these nanoparticles varied from spherical to cylindrical. The possible reason for synthesis of biochar nanoparticles is due to the presence of different biomolecules in plant extracts like alkaloids, terpenoids, flavonoids, sugars and amino-acids which act as stabilizing and capping agents. The reductant chemicals used for different nanoparticle synthesis helps in reduction process. The reason for different shapes and sizes of nanoparticles is due to use of different plant extract and different protocols. Our results are in agreement with the results of Awwad *et al.* (2015) who reported that sulphur nanoparticles synthesized from *Albizia julibrissin* fruit extracts are spherical in shape, also extracts contain compounds that influence the surface properties and interactions of biochar particles leading to reduction in particle size. These compounds could affect factors such as aggregation, dispersion and adhesion forces among the biochar particles resulting in observed size reduction. These findings corroborate with the results obtained by Murthy *et al.* (2020) who revealed that green synthesis nanoparticles of copper and found that these bond with biomolecules of extracts. They further revealed that synthesized copper nanoparticles were in triangular, Cylindrical and spherical in shape.

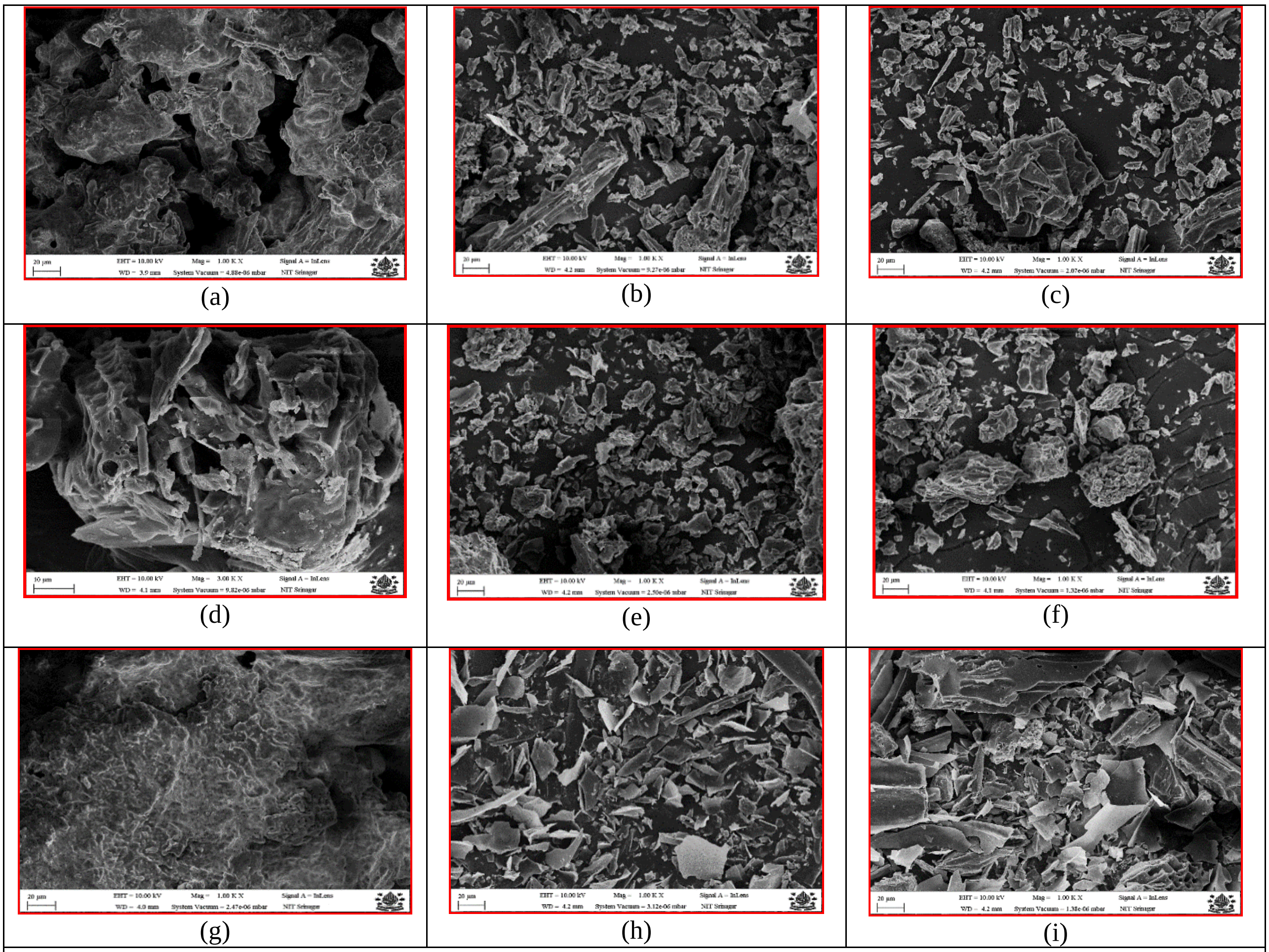
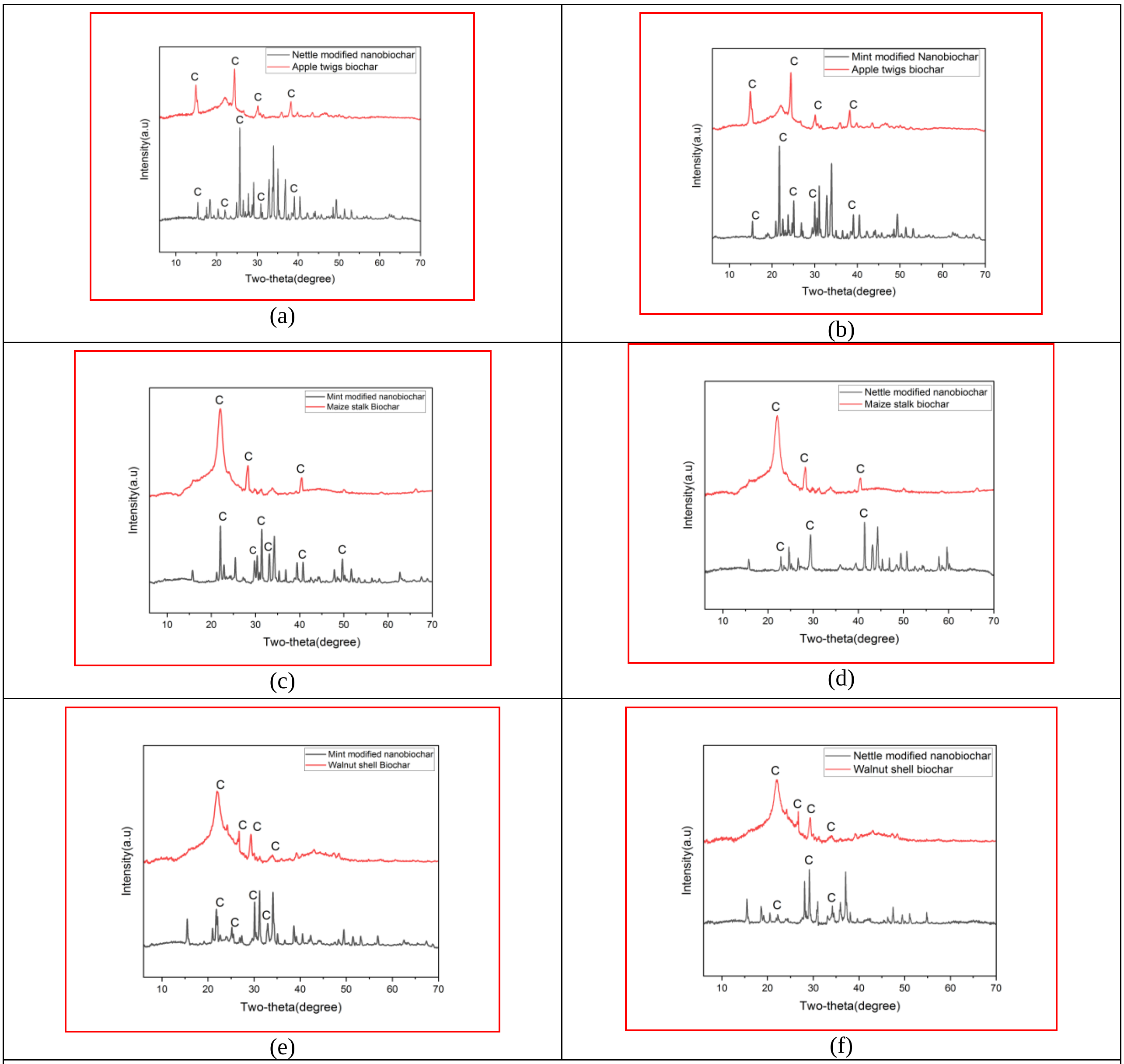

(a) (b) (c)
(d) (e) (f)
(g) (h) (i)

Fig. 1. FESEM micrographs of biochar samples before and after synthesized from mint and nettle extract (a), (d) and (g) are micrographs of Apple twigs, Maize stalk and Walnut shells biochar. Images (b), (e), (h) are nanobiochars synthesized from mint extract and images (c), (f), (i) are nanobiochars synthesized from nettle extract.

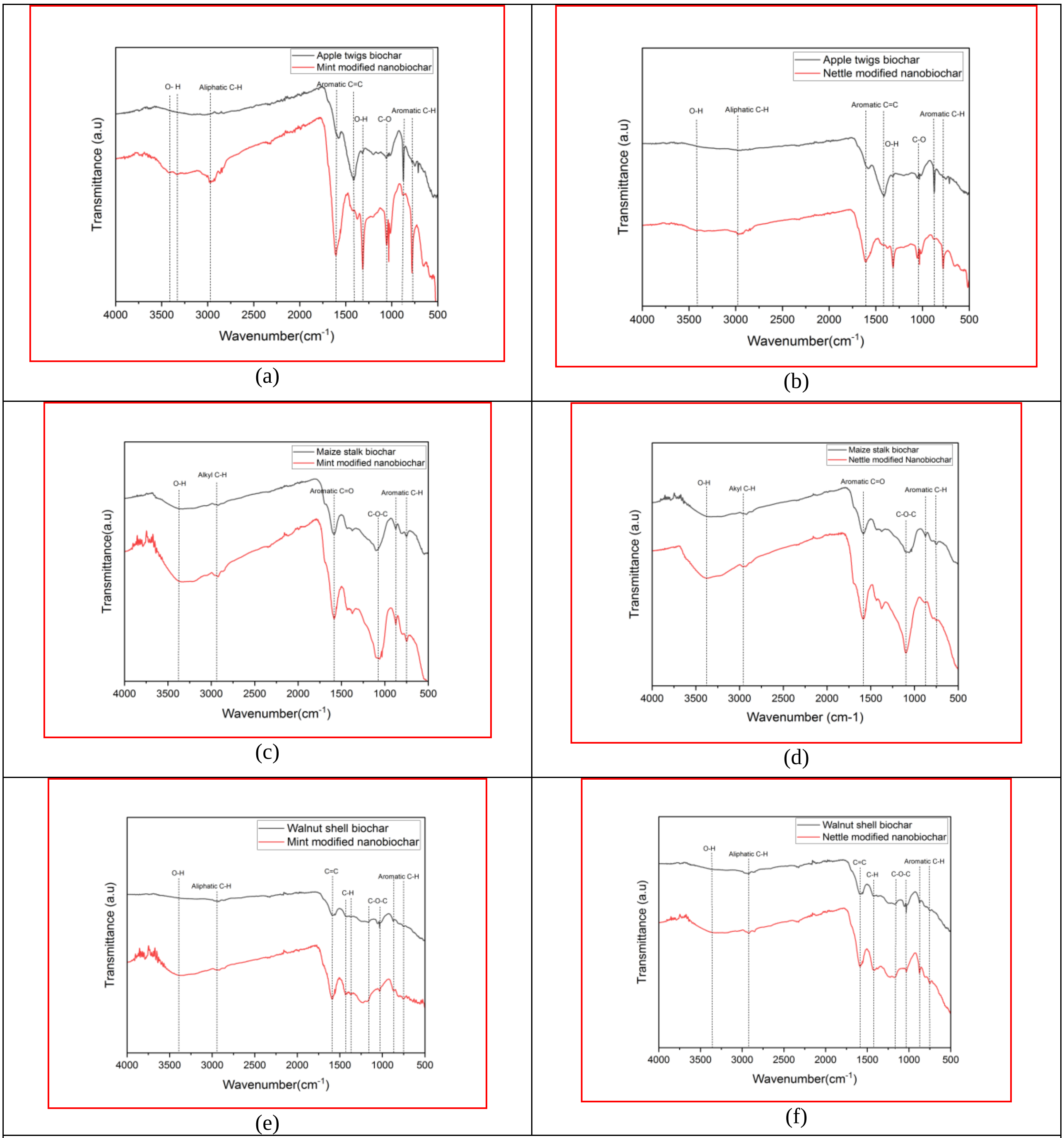
The results XRD analysis were used to detect the existence of various crystals of mineral that can alter biochar properties and hence its applicability. In case of Apple Biochar, the X-ray peaks were found at 2θ = 15°, 24°, 30° and 38° indicated the existence of amorphous and crystalline cellulose in Apple twigs biochar. Furthermore, X-ray diffraction confirmed the presence of Apple twigs biochar which is further consistent with the previous literature available (Liu *et al*., 2022). The peaks at 2θ = 23°, 28°, 41° and 50° from Maize stalk biochar were observed from biochar and compounds containing carbon (Hao *et al*., 2013; Keiluweit *et al*., 2010) while the peaks observed in Walnut shell biochar at 2θ = 22°, 26° and 29° were assigned to cellulose and hemi-cellulose. Alfattani *et al.* (2022) as shown in Fig. 2. All of the nano biochar samples exhibited more intense sharp XRD peaks, shifting and appearance of new peaks was observed, showing that the biochar had a high degree of crystallinity, this is because the mint and nettle extracts contain a variety of organic compounds, such as phenolics, flavonoids, and other functional groups. When these extracts come into contact with biochar, they can react with its surface and potentially form new chemical species or complexes. These new phases can have distinct crystalline structures, leading to the appearance of new peaks in the XRD pattern. Also, these compounds can induce changes in the crystallinity of the biochar. This could be due to interactions between the extract components and the carbon matrix of the biochar, leading to modifications in the arrangement of carbon atoms. Changes in crystallinity can result in shifts or broadening of existing XRD peaks and the appearance of smoother patterns. This is in conformity with the findings of Fakhari *et al*. (2019); Saedi *et al.* (2020) found similar to that reported in case of zinc and sulphur nanoparticles synthesized from *Laurus nobilis* extract.



(a) (b) (c) (d) (e) (f)

Fig. 2. XRD patterns of the Apple twigs, Maize stalk, Walnut shells biochar and their nanobiochars using Mint and Nettle extract.

The effect of the extracts of plants on the surface functional groups of the tested samples of biochar was validated using FT-IR measurements. There were distinct zones that corresponded peak at 3424 cm^{-1} appeared in Apple twigs, Maize stalk and walnut shell biochars is attributed to O-H stretching. The peak at 2935 cm^{-1} is due to aliphatic C–H stretching in case of Apple and walnut biochar. A smaller band from 2800 to 3000 cm^{-1} (peak at 2911cm^{-1}) was likely due to alkyl C-H stretches and a sharp spectral peak at 1594 cm^{-1} was associated with aromatic C=O stretching in Maize stalk biochar. The peak at 1600 cm^{-1} represents the aromatic C=C ring stretching of Apple twigs and Walnut shell biochar. The medium intensity between 1398- 1401 cm^{-1} may be assigned to aromatic skeleton vibrations combined with C-H in Maize stalk and Walnut shell biochar. The peak at 1325 cm^{-1} assigned due to O–H bending and peak intensity at 1100–1030 cm^{-1} due to symmetric C–O stretching in Apple twigs. The peak at 1111 cm^{-1} corresponds to C-O-C stretching in Maize stalk biochar and Walnut shell biochar. Peaks at 781 cm^{-1} are due to pyridine (pyridine ring vibration and C–H deformation) in Apple twigs biochar and 872-748 cm^{-1} are due to aromatic C-H stretching as shown in Fig. 3. This is in agreement with the findings of Zhao *et al*. (2017); Song *et al*. (2016); Alfattani *et al*. (2022). After adding mint and nettle extract stretching pattern of all functional groups was observed. The interactions between the organic compounds and the functional groups in the biochar can lead to enhanced reactivity of the functional groups. The additional interactions can cause changes in the lengths and angles of bonds, resulting in stretching of the functional groups which results an increase in absorbance than transmittance in FTIR spectroscopy. These results get supported from the findings of Gabriela *et al*. (2017) found similar trend to that reported in case of Mint Leaf Extract is utilized in the production of silver nanoparticles.



(a) (b) (c) (d) (e) (f)

Fig. 3. FTIR spectrum of the Apple twigs, Maize stalk, Walnut shells biochar and their nanobiochars using Mint and Nettle extract.

CONCLUSIONS

Green synthesis of Nanobiochar using Mint and Nettle extract showed average particle size of 85.8, 86.6 nm for Apple twig biochar, 80, 82.2 nm for Maize stalk biochar and 105.2,95 nm for Walnut shell biochar confirmed by SEM, XRD and FT-IR. Also, the crystalline structure was observed by XRD. This innovative approach to synthesizing nano biochar through biological means, utilizing Mint and Nettle extracts, holds significant promise for promoting environmentally friendly and sustainable agricultural practices. Beyond its agricultural applications, this method could find broader utility as a dosimeter across various fields, reflecting its versatility and potential to contribute to eco-conscious solutions in multiple industries. The utilization of natural extracts for nano biochar synthesis represents a noteworthy step toward greener and more responsible technological advancements.

Conflict of Interest. None.

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How to cite this article: Rihana Rahman, Javid Ahmad Sofi, Nayar Afaq Kirmani, Ghulam Irshad Hassan Dar, Nageena Nazir, Sheikh Amjid, Tariq Ahmad Sofi, Neelofar Banday, Shaista Nazir, Shahnawaz Rasool Dar, Raqib Majeed Wani and Muneer Ahmad Bhat (2023). Novel Green Approach for the Synthesis of Nano biochar using Plant Resources and Botanical Extracts. *Biological Forum – An International Journal, 15*(9): 887-892.