Eurasian Journal of Agricultural Research 2024; Vol:8, Issue:2, pp:183-191

Sustainable Material Production from Agricultural Wastes: Bio-nano Carbon

Furkan BAŞ[1*], Burak Hakan AKSOY[2]

[1]Biosystems Engineering Department, Agricultural Sciences and Technologies Faculty, Niğde Ömer Halisdemir University, Niğde, Turkiye
[2]Plant Production and Technologies Department, Agricultural Sciences and Technologies Faculty, Niğde Ömer Halisdemir University, Niğde, Turkiye

[*]Corresponding author: furkanbas@ohu.edu.tr

[*]ORCID: 0000-0002-1312-6871

Abstract

Agricultural activities play a key role in the production and supply of the food needed to sustain life. In recent years, agricultural activities have accelerated to meet the food demands of a rapidly growing world population. However, intensive agricultural activities generate a significant amount of waste and by-products. These wastes are mostly composed of organic materials, and if not properly stored, disposed of, or managed, they cause soil-water-air pollution and threaten the environment and public health. Therefore, the recycling of agricultural wastes is of great environmental and economic importance. In addition, recycling agricultural wastes and transforming them into high value-added products by subjecting them to various resource recovery processes contributes to the concept of sustainability and circular economy and provides access to raw materials from local resources in a cheap and easily accessible manner. In this context, in this study, apple and its by-products, which are among the wastes of agriculture and food processing industry, were collected from the apple orchards and apple juice production plant of a company operating in the local region and bio-nano materials were produced from these wastes in a sustainable manner. In the study, the wastes were carbonized using hydro-thermal synthesis method and then reduced to nano size by grinding. FESEM, EDX and XRD analyses were carried out on the carbons produced in the study. The results of the study showed that bio-nano materials can be sustainably produced from agricultural wastes.

Keywords: Agricultural waste, bio-nano material, hydro-thermal synthesis, Resource recovery, sustainability

Research article
Received Date: 8 October 2024
Accepted Date: 23 November 2024

INTRODUCTION

With the development of science and technology, human life has become longer and more comfortable. Due to increased comfort and health facilities, human life has been prolonged, and the population has increased rapidly. The increase in human life expectancy and population growth has rapidly increased the demand for food and energy. To meet this demand, activities in these areas have become more intensive. As a result of these intensive activities, many wastes are generated, and these wastes cause various public health and environmental problems. The main environmental problems are soil-water-air pollution, release of toxic substances and heavy metals, pH imbalance in soil and water, damage to ecosystems, risk of species extinction and inefficiency of agricultural land.

Waste management is critical to minimizing or eliminating these environmental impacts. Through recycling processes, resource recovery and circular economy concepts, both environmental and economic benefits can be achieved by recovering these wastes and transforming them into high value-added products. In addition, it aims to contribute to sustainability by supporting concepts such as green economy, resource recovery and recycling through various plans, programs, policies and strategies (Dehkordi et al., 2024).

Hydrothermal synthesis is a carbonization process that takes place under high pressure and temperature, allowing the upcycling of agricultural waste. Hydrothermal synthesis is widely used to produce carbon materials, biofuels and other valuable products from biomass. Due to their high organic and carbon content, agricultural wastes are highly suitable sources for carbon production by hydrothermal synthesis. However, various wastes are generated as a result of agricultural activities and the contents of these wastes vary (Zamani et al., 2019). In this direction, the types of agricultural wastes to which hydrothermal synthesis parameters can be applied are discussed as follows:

I. Wastes with high content of cellulose and lignocellulose:
Lignocellulosic biomasses such as wood chips, corn stalks and rice husks are highly suitable wastes for hydrothermal synthesis. Such wastes allow to obtain hydrocarbon-rich products thanks to the lignin, cellulose and hemicellulose in their structure. Under high temperature (180-250°C) and pressure, these components can be decomposed into carbon-based materials.

II. Waste with low carbon content:
Biomasses with high moisture content and low carbon content, such as fruit and vegetable wastes, are not suitable for hydrothermal synthesis. Such wastes reduce the energy efficiency due to their high water content and can negatively affect the quality of the target products (e.g. hydrocarbons, carbon materials). However, these wastes can be included in the process after pre-drying or concentration.

III. Tailings with high protein and fat content:
Wastes from the food processing industry (e.g. meat, fish, dairy wastes) often contain proteins and fats. The use of such wastes in hydrothermal synthesis can lead to the formation of by-products (e.g. ammonia, fatty acids). As this can adversely affect the purity of the carbon structures, the usability of such wastes is limited.

IV. Wastes Containing Toxic and Inhibitory Substances:
Pesticide residues or agricultural wastes containing heavy metals should not be used in hydrothermal synthesis. Such substances can damage process equipment and reduce the quality of the resulting products. They may also pose environmental and health risks.

V. Fibrous and heterogeneous wastes:
While fibrous and heterogeneous biomasses such as cotton stalks and sunflower stalks are suitable for hydrothermal synthesis, process efficiency must be optimized. Pretreatments such as shredding and grinding allow for more efficient conversion of such wastes in a homogeneous reactor environment.

Hydrothermal synthesis is a suitable process for agricultural wastes with high carbon content and low moisture content. However, the choice of process parameters (temperature, pressure, time, catalyst usage) should be optimized according to the type of waste. For wastes with high moisture content or containing inhibiting substances, pre-treatment processes are required.

Therefore, the applicability of hydrothermal synthesis depends on both the physicochemical properties of the waste and the type of product to be produced (Fathy et al., 2020).

Bio-nano materials are defined as nanometer-sized materials inspired by biological systems or obtained by direct use of biological structures. These materials generally have a physical and chemical structure that can interact with biological organisms, are biocompatible, or simulate biological functions. Due to their nanoscale properties, bio-nano materials are used in many fields such as agriculture, energy, environment, construction, medicine, chemistry and food industry (Gado, 2022).

Bio-nano materials can be produced by various physical, chemical and biological methods. These methods can be basically listed as top-down, bottom-up, biosynthetic methods, chemical vapor deposition and carbonization. Bio-nano materials have the potential to make a significant contribution to sustainability. The raw materials needed to produce biomaterials are usually biomass resources, and they enable the production of environmentally friendly and recyclable materials using natural biological processes. For example, biodegradable alternative materials can solve the problem of plastic waste. At the same time, bio-nano materials that increase energy efficiency and are used in renewable energy technologies can provide environmentally friendly solutions by replacing fossil fuels. In terms of sustainability, bio-nano materials offer advantages with their environmentally friendly production processes, energy efficiency and recyclability (Rasool et al., 2024).

Bio-nano-carbon materials contain carbon structures in which carbon atoms are organized at the nanoscale and are inspired by biological processes or produced from biomass-based sources. These materials can generally be listed as carbon nanotubes (CNT), graphene, carbon nanofibers (CNF), carbon dots (CDs). Due to their chemical, physical and biological properties, these materials have important applications especially in areas such as construction, energy storage, catalysis, sensors, medical and environmental engineering (Huang et al., 2021).

Bio-nano-carbon materials can be produced using biological processes as well as traditional manufacturing techniques. These production methods can be listed as Chemical Vapor Deposition (CVD), Biomass Derived Carbonization, Hydrothermal Carbonization and Electrospinning. These methods are basically the same, but the process details and input parameters differ. Bio-nano carbon materials contribute greatly to sustainability in terms of raw materials, production methods and applications. Carbon nanomaterials produced from sustainable biomass sources can be used as an alternative to fossil fuel-based carbon materials and can reduce the carbon footprint (Goswami et al., 2024).

In the study, apples and their by-products, which are commonly used in the agricultural and food processing industries, were selected as the biomass source and supplied by a local company. They were then subjected to different carbonization processes and their material properties were studied with different analyses.

MATERIAL and METHOD

In this study, apples and wastes used as raw materials for the bio-nano carbon production were obtained from the apple orchards and factory outlets of a company operating in the region, which is engaged in both apple growing and fruit juice production from the apples it grows.

The wastes were subjected to physical pretreatments. First, the waste was thrown into a shredder and then passed through a screen with a mesh size of 60-80 mesh. Apples and wastes subjected to physical pretreatment are shown in Figure 1. At the end of the physical pre-treatment, the apple waste was separated from hard-to-carbonize materials such as stalks, seeds and peels, and brought to a more homogeneous structure.

Figure 1. Apple wastes after physical treatment.

After the physical pretreatment, the finished waste was dried for 24 hours in an oven set at 105ºC. At this stage, the moisture and water in the waste were removed and the dried waste was then transferred to the hydrothermal synthesis reactor. Carbonization of biomass to high surface area particle sizes was achieved for 6 hours at a temperature of 250 ºC, which was determined as a result of literature studies (Correa et al., 2017; Zhao et al., 2018). The carbon produced at this stage was synthesized as carbonized biomass with large particle sizes. As part of the study, a Fritsch Pulverisette 6 ball mill was used to reduce the size of the carbonized material to nano sizes. The size reduction process with the ball mill was carried out at a maximum frequency of 35 Hz, a maximum operating speed of 650 rpm, a centrifugal acceleration of 29 g, and a minimum time of 3 hours. The size of the material obtained after the size reduction process with the ball mill at the specified parameters was aimed to be < 1 µm. Bio-nano carbon synthesis scheme can be seen in Figure 2.

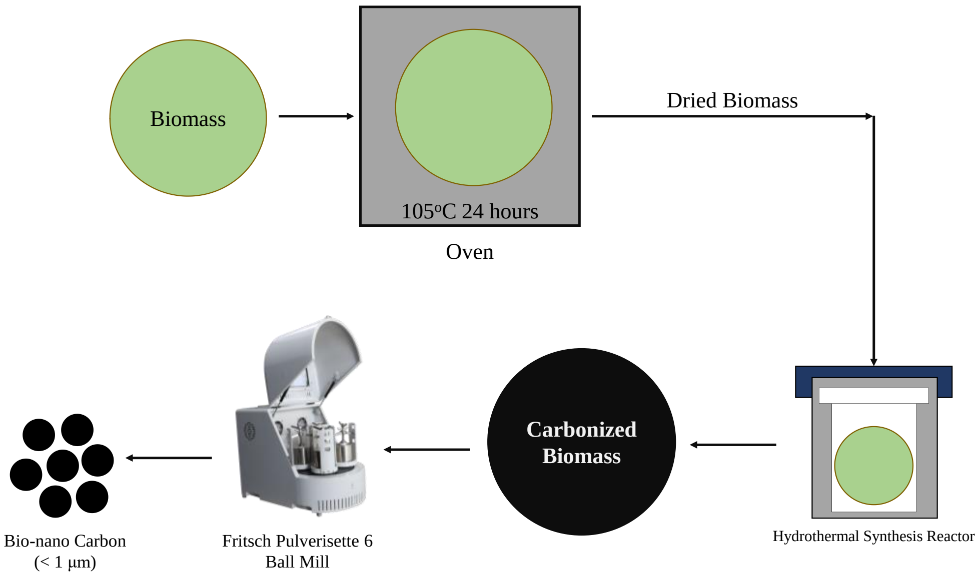

Figure 2. Bio-nano carbon synthesis scheme.

In the last step, FESEM images of the material obtained after the size reduction process were taken and the physical properties of the nanomaterial were analyzed. In addition, the morphological structure of the material was further investigated by EDX and XRD analysis.

RESULTS and DISCUSSION

The results of the study showed that biomass from apple waste was successfully used for bio-nano-carbon production. Homogenization of the waste by physical pre-treatment and removal of moisture prior to carbonization increased the efficiency of the carbonization process. The hydrothermal carbonization process, which was performed at 250 °C for 6 h according to the literature, allowed the biomass to be carbonized in large particle sizes. This step demonstrated that apple waste is suitable for the production of carbon structures even at low temperatures.

The ball milling process carried out after carbonization succeeded in reaching nano sizes using a Fritsch Pulverisette 6 ball mill. With a frequency of 35 Hz, a speed of 650 rpm, and a centrifugal acceleration of 29 g, the particle size was reduced to <1 μm during a total grinding time of 3 hours. This result shows that the grinding parameters were correctly selected and effective in producing nanostructures.

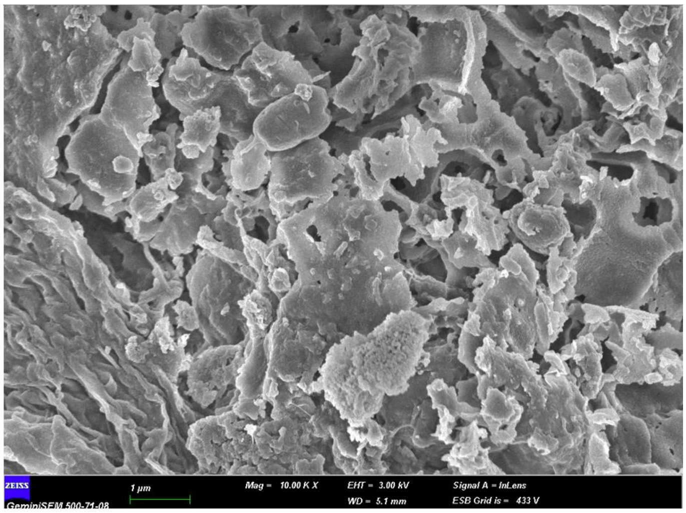

Figure 3. FESEM images of carbonized apple waste.

The physical and morphological properties of the obtained nanocarbon were analyzed using advanced imaging techniques. FESEM images taken under the parameters Mag= 10.00 K X, EHT= 3.00 kW, WD= 5.1 mm. FESEM imaging (Figure 3) revealed that the surface morphology of the obtained nanocarbon is highly homogeneous and well dispersed. In addition, temperature-dependent cracks, fractures and distortions can be observed on the surface of the material. These results indicate the effects of physical pretreatments and grinding parameters on the structural integrity of the material (Konovalova, 2021). Figure 4 shows the graphs of the EDX and XRD analyses. The EDX analysis revealed the elemental composition of the nanocarbon, confirming that the carbon content is rich, and the impurity level remains low. Moreover, the results obtained by XRD analysis showed that the crystalline structure of the material was successfully transformed into carbon structure and the formation of amorphous carbon was limited (Sabet and Mahdavi, 2019).

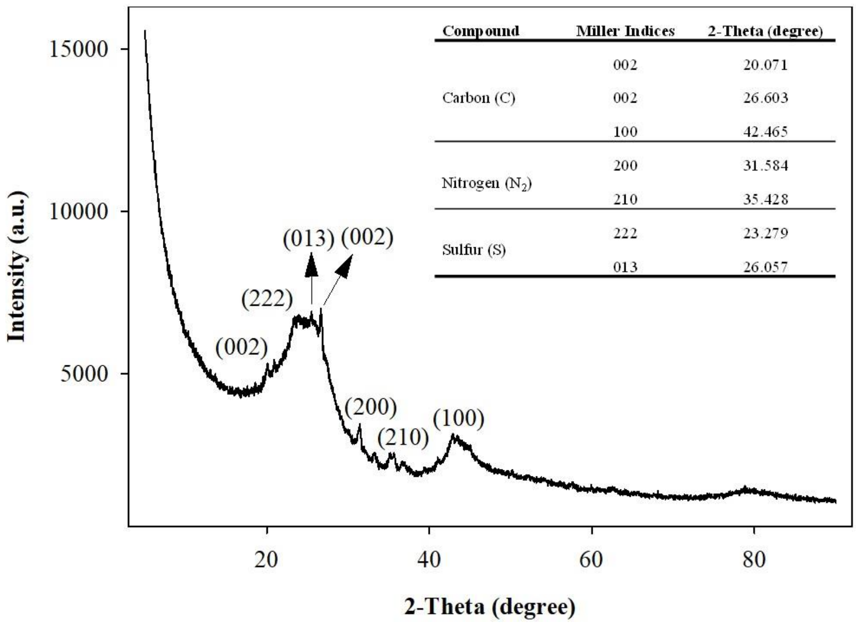

Figure 4. EDX and XRD mapping.

In Figure 4, carbon (C) peaks are observed at Miller indices 002, 002, 313 at 20.404, 26.603, 41.666 degrees, respectively. In addition, a CO_2 peak was found at Miller Index 110 and 22,313 degrees. The presence of CO_2 can be explained by the atmospheric conditions under which the samples were stored up to and during the analysis. The N_2 peak is observed at Miller Index 101 and at 28.509 degrees, and the presence of the N_2 peak can also be explained by atmospheric conditions. The analyses also found additional SiO_2 peaks at Miller indices 112 and 202 and at 31.362 and 36.191 degrees, respectively. The presence of SiO_2 is a common occurrence in studies of carbon produced from biomass. The elements C and Si are abundant in nature and in biomass-derived sources, and both elements are chemically very close to each other (Chen et al., 2022). For this reason, the element Si and the compounds formed by this element are often found on activated carbon in XRD analysis (Fekri et al., 2022).

The XRD pattern shows well-defined peaks corresponding to carbon (C), nitrogen (N), and sulfur (S) phases, with specific Miller indices indicating crystallographic orientations such as (002), (013), (100), and others. The presence of crystalline phases is evidenced by sharp peaks, but the lower-intensity peaks may suggest the existence of amorphous regions or minor crystallinity. Surface cracks often disrupt the regular crystal structure, leading to peak broadening or reduced intensity in XRD patterns. These defects can decrease crystallinity and alter the mechanical integrity of the material. Carbon-based materials with sulfur and nitrogen doping, like those indicated here, are promising in applications such as energy storage (e.g., supercapacitors or batteries) or catalysis. However, cracks could impact conductivity and mechanical stability, which might limit their use in structural applications but enhance their catalytic or adsorption performance.

FESEM imaging is crucial to confirm the presence, distribution, and extent of surface cracks. If cracks are numerous or deep, they may compromise the material's structural stability but could increase the surface area, which is beneficial for catalytic or energy storage applications. Uniform and minimal cracks could indicate better mechanical properties, making the material suitable for structural applications.

High crack density, especially with sharp-edged cracks, might indicate brittleness but provide pathways for ion transport, enhancing electrochemical performance.

EDX analysis can validate the elemental composition identified in the XRD, particularly the distribution of sulfur, nitrogen, and carbon. Uniform elemental distribution would support the presence of homogeneous phases, while segregation might imply localized defects. Cracks could expose the material to the environment, leading to oxidation or contamination, which may affect the elemental composition detected in EDX. Elemental mapping from EDX could help determine whether cracks alter the uniformity of the material's composition.

Surface cracks, if extensive, could lower the material's mechanical strength, limiting its application in load-bearing environments. Cracks may enhance specific applications like supercapacitors or batteries by increasing the surface area for charge transfer and enhancing ion accessibility. Cracks may improve catalytic activity by exposing more active sites, especially if the material's elemental composition (e.g., N and S doping) supports catalytic properties. Surface cracks could hinder electron transport in applications requiring high conductivity unless the cracks are minimal, and the material maintains a continuous crystalline network.

CONCLUSION

In the current study, bio-nano-carbon materials were successfully prepared from apple waste by the hydrothermal synthesis method. The recovery and utilization of agricultural wastes is of great importance both in terms of sustainable material production and circular economy. Apple waste, which usually has low economic value as a by-product of agriculture and food industry, was transformed into high value bio-nano-carbon materials by the processes applied in this study. This approach is an important example of efficient use of resources and strengthening of waste management policies.

Considering the contribution of the study to sustainability, the recycling and reuse of biomass contributes to the reduction of environmental pollution. While the disposal of biological wastes usually represents a significant cost and environmental risk in waste management processes, the conversion of these wastes into high-tech materials contributes to the reduction of the carbon footprint and reduces the consumption of natural resources. The use of apple waste in the production of bio-nano-carbon provides an effective method for the utilization of renewable resources and contributes to the development of sustainable production strategies.

In the context of the circular economy, the conversion of apple waste into bio-nano-carbon material is an important contribution to the development of closed-loop production processes as an alternative to linear production models. In this process, the recycling of waste materials into valuable products not only provides economic benefits, but also supports the efficient use of resources by reducing the need for raw materials. Particularly in light of developments in nanotechnology and materials science, the integration of biomass resources such as apple waste into advanced technologies enables the development of innovative products.

This study demonstrates that high value-added products can be obtained from waste and that food industry by-products can be converted into innovative and environmentally friendly materials. Bio-nano-carbon from apple waste has the potential to be used in a wide range of applications. For example, in energy storage, these materials could be tailored for use in supercapacitors or as electrodes in batteries, taking advantage of their high surface area and conductivity. In addition, bio-nano-carbon materials could play an important role in environmental purification technologies, such as water filtration systems, due to their porous structure and adsorption properties. Exploring these specific applications can help bridge the gap between laboratory-scale research and real-world implementation.

In the future, the applicability of such approaches on a larger scale will contribute significantly to the development of sustainable production and recycling processes. Further research could focus on optimizing the properties of bio-nano-carbon materials to improve their performance in energy and environmental applications, as well as investigating their economic feasibility and scalability.

ACKNOWLEDGMENT

This project was supported by TÜBİTAK - 2209B University Students Industrial Research Projects Support Program with project code 1139B412300005.

REFERENCES

Dehkordi M. M., Nodeh Z. P., Dehkordi K. S., Khorjestan R. R., & Ghaffarzadeh M. 2024. Soil, air, and water pollution from mining and industrial activities: sources of pollution, environmental impacts, and prevention and control methods. Results in Engineering, 102729.

Chen K., Ng K. H., Cheng C. K., Cheng Y. W., Chong C. C., Vo D. V. N., ... & Ismail M. H. 2022. Biomass-derived carbon-based and silica-based materials for catalytic and adsorptive applications-An update since 2010. Chemosphere, 287, 132222.

Correa C. R., Bernardo M., Ribeiro R. P., Esteves I. A. & Kruse A. 2017. Evaluation of hydrothermal carbonization as a preliminary step for the production of functional materials from biogas digestate. Journal of Analytical and Applied Pyrolysis, 124, 461-474.

Fathy N. A., Basta A. H. & Lotfy V. F. 2020. Novel trends for synthesis of carbon nanostructures from agricultural wastes. In *Carbon nanomaterials for agri-food and environmental applications* (pp. 59-74). Elsevier.

Fekri M.H., Tousi F., Heydari R., Razavi Mehr M., Rashidipour M. 2022. Synthesis of magnetic novel hybrid nanocomposite (Fe3O4@ SiO_2/activated carbon (by a green method and evaluation of its antibacterial potential. Iranian Journal of Chemistry and Chemical Engineering, 41(3), 767-76.

Goda E. S. 2022. Bio-nanomaterial for renewable energy storage applications. In Biorenewable Nanocomposite Materials, Vol. 1: Electrocatalysts and Energy Storage (pp. 91-127). American Chemical Society.

Goswami A. D., Trivedi D. H., Jadhav N. L. & Pinjari D. V. 2021. Sustainable and green synthesis of carbon nanomaterials: A review. Journal of Environmental Chemical Engineering, 9(5), 106118.

Huang H., Feng W. & Chen Y. 2021. Two-dimensional biomaterials: material science, biological effect and biomedical engineering applications. Chemical Society Reviews, 50(20), 11381-11485.

Konovalova V. 2021. The effect of temperature on the corrosion rate of iron-carbon alloys. Materials Today: Proceedings, 38, 1326-1329.

Rasool A., Sri S., Zulfajri M. & Krismastuti F. S. H. 2024. Nature inspired nanomaterials, advancements in green synthesis for biological sustainability. Inorganic Chemistry Communications, 112954.

Sabet M. & Mahdavi K. 2019. Green synthesis of high photoluminescence nitrogen-doped carbon quantum dots from grass via a simple hydrothermal method for removing organic and inorganic water pollutions. Applied surface science, 463, 283-291.

Zamani A., Marjani A. P. & Mousavi Z. 2019. Agricultural waste biomass-assisted nanostructures: Synthesis and application. *Green Processing and Synthesis, 8*(1), 421-429.

Zhao X., Becker G. C., Faweya N., Rodriguez Correa C., Yang S., Xie X. & Kruse A. 2018. Fertilizer and activated carbon production by hydrothermal carbonization of digestate. Biomass Conversion and Biorefinery, 8, 423-436.