MME SEE CONGRESS 2023

5th Metallurgical & Materials Engineering Congress of South-East Europe
Trebinje, Bosnia and Herzegovina
7-10th June 2023

CONGRESS PROCEEDINGS

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CHARACTERIZATION OF RAW PEACH STONES AND ITS BIOCHAR BY SEM, FTIR AND RAMAN SPECTROSCOPY

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Growing industrialization and non-renewable resource depletion have a huge impact on alternative clean up technologies development, inducing investigation of the renewable, low-cost waste materials. Recently, lignocellulosic waste biomass, generated at a large scale by different industries, appeared as an attractive feedstock worldwide, due to its abundance, availability, multi-functionality and low cost. Since the fruits production has increasing trend all over the world, generation of lignocellulosic waste such as fruit stones (that represent approximately 1/5 of the total fruit mass) became a great environmental threat. In order to minimize negative impact on the environment, avoid greenhouse gasses emissions and help in resource depletion by its renewable nature, it is necessary to explore its performances regarding its wide application potential. Thermo-chemical conversion of lignocellulosic biomass in oxygen limited conditions, in order to get biochar, has received a lot of attention recently. The biochar production requires lower energy inputs and less expensive technology compared to activated carbon (estimation is that production cost of activated carbon are six times higher than biochar costs).

In this paper, waste peach stones biomass was effectively converted into biochar at 500 °C under inert (Ar) atmosphere. Pyrolysis was performed in Nabertherm 1300 muffle furnace for residence time of 1.5 h, with a heating rate of 10 °C/min, while Ar was circulated through the sample at a rate of 100 mL/min. The raw biomass (PS) and obtained biochar (PS-B) with particle size 0.1 mm < d_p < 0.5 mm, were characterized by Scanning Electron Microscopy (SEM), Fourier transform infrared spectrometry (FTIR) and Raman spectrometry to understand physicochemical changes which have been occurred after pyrolysis. SEM analysis revealed the increased surface area due to the visible augmentation of pores and roughness. FTIR analysis showed that many bands present in native biomass cannot be observed in biochar, due to the conversion or removal of the most of the functional groups. Prominent bands have confirmed presences of aromatic compounds in biochar: at 1592 cm^{-1} (C=C bond stretching derived from aromatic rings in the lignin), 1030 cm^{-1} (alcohol C-O stretching vibration) and in the region 900 to 700 cm^{-1} (originating from aromatic compounds). These finding are in accordance with results from Raman analysis, where D and G bands (at 1350 cm^{-1} and 1580 cm^{-1} respectively), indicate the presence of poly-aromatic hydrocarbons.

Thermo-chemically modified biomass like this has a great application potential: as a pollutants sorbent, biofuel, soil amendment, biocarriers, and in construction and electronic industries.

Keywords: peach stones; pyrolysis; biochar; SEM; FTIR; Raman.

Introduction

Biochar is a type of charcoal that is produced by slow heating of organic materials, such as agricultural waste, wood, or manure, in the absence of oxygen. The process, known as pyrolysis, transforms the organic materials into a carbon-rich material that is resistant to decomposition and can be used as a soil amendment or a source of renewable energy. Biochar production has gained increasing attention in recent years, due to its potential to address several environmental challenges. For example, biochar can be used to sequester carbon and reduce greenhouse gas emissions, improve soil fertility and structure, and reduce water pollution (Chee et al., 2012).
The characteristics of biochar depend on the type of feedstock used, the pyrolysis temperature and contact time, as well as the production method. Generally, biochar has a high surface area, which makes it an effective adsorbent for nutrients and contaminants in soil and water (Lopičić et al., 2021). It also has a stable carbon structure that can remain in soil for centuries. The utilization of biochar can vary depending on the intended application. In agriculture, biochar can be used as a soil amendment to improve soil structure, water retention, and nutrient availability.

It can also be used as a livestock feed supplement to improve animal health and reduce greenhouse gas emissions from manure. In addition, biochar can be used as a renewable energy source for heating and electricity generation. Overall, biochar offers a promising solution for sustainable waste management and soil improvement. With continued research and development, biochar production and utilization could become an important tool for mitigating climate change and promoting sustainable agriculture.

Biochar production from agricultural waste, such as fruit stones, can help mitigate greenhouse gas emissions and provide a sustainable source of soil amendment. Raw peach stones are a common byproduct of the food industry, and have been identified as a potential feedstock for biochar production. In this study, we have characterized the raw peach stones and its biochar using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy. Our objective is to investigate the structural and chemical changes that occur during pyrolysis and evaluate the potential of peach stone biochar for various applications such as soil amendment, pollutants sorbent, biofuel, biocarriers, etc. This study provides a comprehensive characterization of raw peach stones and its biochar, which can aid in the development of sustainable biochar production methods and facilitate the utilization of agricultural waste for environmental benefit.

Materials and methods

Materials

A peach stones were collected from fruit processing industry „Vino Župa" (Aleksandrovac, Serbia). Collected samples were further washed, dried and grounded using a vibratory disk mill "Siebtechnik – T S250" (Siebtechnik GmbH, Germany). The obtained sample was sieved at particle size 0.1 mm < dp < 0.5 mm. This sample was labeled as PS.

Pyrolysis of PS

Pyrolysis of the PS were performed in Nabertherm 1300 muffle furnace (Nabertherm, Germany) at 500 °C for residence time of 1.5 h, with a heating rate of 10 °C/min. Argon was circulated through the sample at a rate of 100 mL/min. The obtained biochar was labeled as PS-B.

Characterization of PS and PS-B

The morphology of both samples (raw and pyrolyzed samples) was analyzed by Scanning Electron Microscopy (SEM), using a JEOL JSM-6610 LV SEM model (JEOL Ltd. Japan), while Thermo Nicolet 6700 FTIR (International Equipment Trading Ltd. USA) with an attenuated total reflectance (ATR) module (in the range of 400–4000 cm-1) was used to investigate functional groups on its surfaces. Raman confocal microscope (Raman alpha300R, WITEC, GMBH, GERMANY) (Wavelength 532 nm, 24 mW power) was employed for obtaining Raman spectra. During the spectral recording, the laser was focused onto the sample on the microscope stage through a 50X objective (Zeiss, 0.7 N.A.). Raman scattered photons were collected through a 50 µm fiber and directed to a 300 mm spectrograph equipped with 600 gr/mm grating and thermo-cooled CCD. The spectral resolution was about 1 cm^{-1} and the calibration was checked by a 520.47 cm^{-1} line of silicon.

Results and discussion

Peach stones are lignocellulosic material made of cellulose, hemicelluloses and lignin. Such material is suitable for conversion into carbon rich material (biochar) by thermochemical process (pyrolysis) which takes place above 300 °C (Debevc et al., 2022).

Pyrolysis can convert biomass into three end-products: syngas, bio-oil, and biochar. Biochar is of

great interest in last decades due to the diverse application potential. Factors such as feedstock, heating rate, pyrolysis temperature and residence time determine yield and physicochemical properties of the biochar (Debevc et al., 2022).
In order to observe changes that has occurred on raw material after pyrolysis and to scan the surface morphology of the both samples, SEM analysis was used at a magnification of 500x (Figure 1). SEM micrographs showed that raw sample (Figure 1a) has a rough and amorphous structure, with cavities and clogged pores, which is primarily consequence of compression effect onto material during milling. During the process of pyrolysis bond breaking of hydrocarbons in biomass occurs, as well as release of volatile substances, resulting in highly developed porous biochar surface. SEM micrograph of biochar PS-B showed much complex structure which is presented by smaller pores and rougher surface, indicating an increased surface area (Figure 1b). Indeed, the BET analysis the specific surface area has increased from 0.545 $m^2 g^{-1}$ (PS) to the value of 159.1 $m^2 g^{-1}$ (PS-B) after the thermal with more than 10 times decrease in pore diameter (Lopičić et al., 2021).

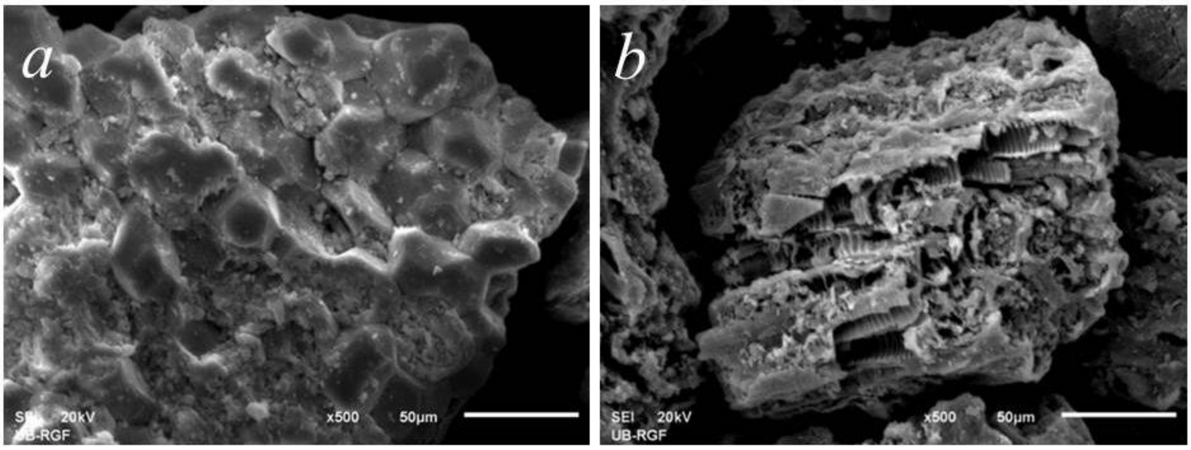

Figure 1 SEM micrographs of the (a) PS and (b) PS-B

The Fourier transform infrared spectrometry analysis was used to determine functional groups present in both samples; the spectra for PS and PS-B are shown in Figure 2.

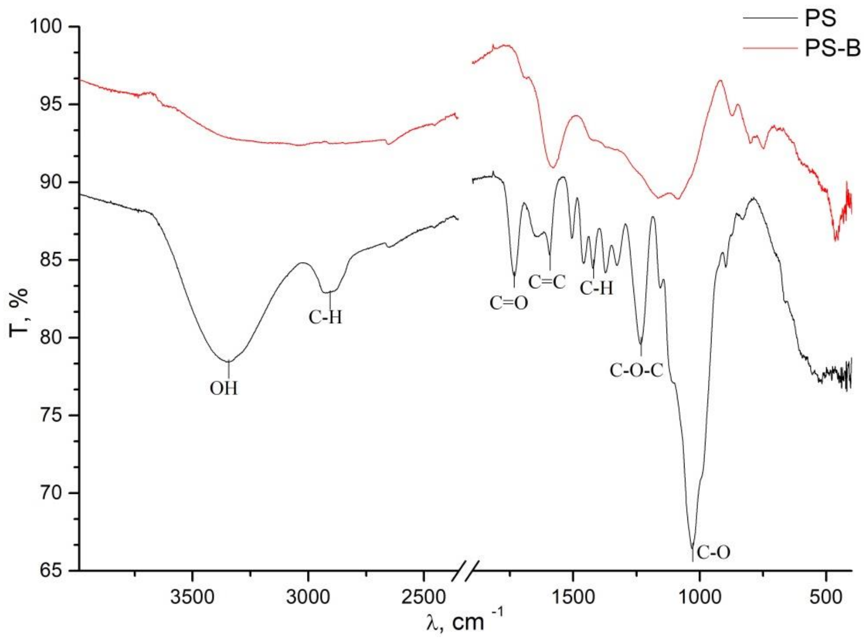

Figure 2 FTIR spectra of PS and PS-B

Analysis of both FTIR spectra showed that many bands present in PS cannot be observed in PS-B, indicating that most functional groups are either converted or disappeared after pyrolysis. After pyrolysis some of the -OH groups from cellulose remain in the sample, which is evident in the Figure 2 (band at 3340 cm^{-1} assigned to OH stretching). Also, band at 2920 cm^{-1} (aliphatic C-H stretch) confirms that the cellulose is not entirely carbonized during pyrolysis (Chee et al., 2012). Band at 1736 cm^{-1} (C=O stretching) indicate the presence of a variety of functional groups such as ketones, carboxylic acids esters, and anhydrides, while band at 1592 cm^{-1} is assigned to C=C bond stretching derived from aromatic rings (benzene ring) in the lignin (Chee et al., 2012). Since this band still can be observed in sample PS-B, it is clear that lignin is still present after thermal treatment. Also, the peak height of the band at 1373 cm^{-1} (C-H stretching) is much lower than in raw PS sample, indicating that hemicellulose has been significantly decreased. Alcohol C-O stretching vibration is confirmed by the presence of band at 1030 cm^{-1}. Bands in the region 900 to 700 cm^{-1} are also observed in PS-B sample, originating from aromatic compounds (Lopičić et al., 2021). As it can be seen from Figure 2, the evolution of aromatic functional groups (PS-B) has replaced aliphatic groups of raw biomass (PS), since the aliphatic radicals rich in oxygen from lignin and hemicellulose are nearly entirely volatilized while the carbon chains that remain in the material are reorganized in poly condensed aromatic structures.

Raman spectroscopy has been performed in many studies concerning biochars, but a number of challenges must be overcome to obtain a usable spectrum in Raman spectroscopy. The vibrational peaks have tendency to be masked by the presence of strong fluorescence, due to the presence of polycyclic aromatic compounds that are form after pyrolysis (Chee et al., 2012). According to this group of authors, the reduction of fluorescence can be overcome by use of longer wavelength excitation sources with of localized heating and damaging of the sample. However, the D and G peaks, unique to Raman scattering, are strong enough to permit observation of carbon structural state formed during pyrolysis (Chee et al., 2012). As can be seen in Figure 3, D and G peaks at 1350 cm^{-1} and 1580 cm^{-1}, respectively, assigned to poly-aromatic hydrocarbons are clearly visible. G peak represents vibrations of sp2 carbon atoms found in graphitic materials and double bonds, while the D peak is linked to the breathing modes of disordered graphite rings (Ferrari A., and Robertson J., 2000).

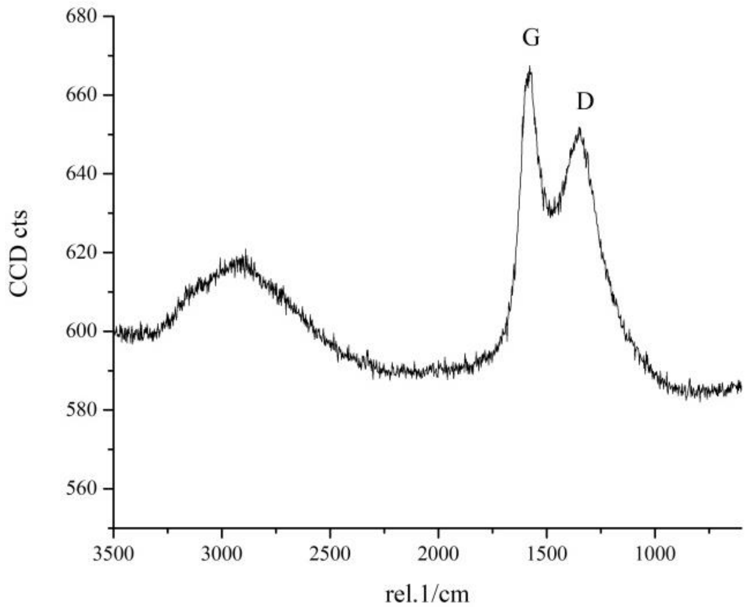

Figure 3 Raman spectra of PS-B

Conclusion

This study deals with characterization of challenging materials such as lignocellulosic biomass (peach stones) before and after process of pyrolysis, by using scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy in order to understand physicochemical changes which have been occurred. Increased surface area after pyrolysis was confirmed by results of SEM analysis, while changes in functional groups were confirmed by results of FTIR analysis: many bands which have been presented in native biomass could not be observed in biochar. Presences of aromatic compounds in biochar were confirmed by bands at 1592 cm^{-1} (aromatic rings in the lignin), 1030 cm^{-1} (alcohol C-O stretching vibration) and in the region 900 to 700 cm^{-1} (aromatic compounds). These were in accordance with Raman analysis results, where D (at 1350 cm^{-1}) and G (1580 cm^{-1}) bands are indicators of the presence of poly-aromatic hydrocarbons.

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