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BIOCHAR AS EFFICIENT TOOL FOR SOIL AMMENDEMENT

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Abstract

Food production generates significant amounts of waste, especially in fruits and vegetables processing industries (FVPI), where biodegradable lignocellulosic waste (LCW) represents approx. 25-30% of processed raw materials. In most cases, this type of waste is landfilled, representing unsustainable practices with significant environmental hazards. Biochar, a highly carbonaceous organic material obtained from thermochemical conversion of LCW biomass, pose significant positive characteristics with multifunctional purpose. Biochar application might remove emerging contaminants from wastewater, and its application on soils improves soil properties such as fertility leading to improved crop productivity, soil pH regulation and soil CEC improvement, as well as microbial activities enhancement. In this paper, the characterization of biochar obtained via slow pyrolysis of peach stone (PS) is done along with its possible application as a soil amendment. This preliminary investigation revealed that the properties of the biochar produced from PS are in line with those necessary to act as a suitable agent for soil amendment.

Keywords: lignocellulosic waste, peach stone, biochar, soil amendment, circular economy.

Introduction

In the European Thematic Strategy for Soil Protection, the EC has recognized the main threats to the soil in the EU. These hazards are marked as loss of soil organic matter, soil compaction, erosion, desertification, salinization, soil acidification, loss of biodiversity, landslides and soil contamination (European Commission, 2020). Soil contamination can be a trigger for other degradation processes because it affects the ecosystem and causes toxicity to organisms, reducing biodiversity, which is associated with the loss of organic matter in the soil, imbalance of nutrients and consequent soil erosion. Regardless of the technology that pollutes the environment, improper disposal of waste or an accident, the land becomes first which is affected by contamination. Pollution spreads quickly through all mediums of the environment, into groundwater or surface water and ultimately affects the health population (SEPA, 2018). Accordingly, the only way to solve existing environmental problems, as well as related health problems, represents remediation of contaminated soil, maintaining and improving soil quality and preventing further contamination. Therefore, in order to sustain soil productivity, the crucial challenge is to maintain adequate levels of organic matter in the soil to preserve its physical, chemical and biological integrity.
Biochar is the product of biomass pyrolysis, a process whereby organic substances are broken down at temperatures ranging from 350 °C to 700 °C in a reduced oxygen thermal process. According to Lehmann and Stephen (2009), biochar applications have an effect on soil improvement, waste management, climate change mitigation and energy, and consequently might have social and economic benefits. Biochar improves soil physiology and increases productivity, assisting with crop

residue management. It also reduces soil acidity, while the essential mineral uptake increases. The significant quantities of K and phosphorus and lower amounts of Mg, Ca, Cu, Zn and Fe, which are presented in biochar, reflects its potential to be applied as fertilizer, too (Mwampamba et al., 2013). Globally, biochar has been considered a soil amendment tool, due to its suitable cation exchange capacity (CEC), which improves the soil pH, water-holding capacity and affinity for plant nutrients (Nsamba et al., 2015). In addition, biochar plays an important role in improving soil health by increasing crop yield and absorbing atmospheric carbon dioxide (Srinivasarao et al., 2013).
Demand for food has drastically increased in the last decades. This has consequently increased the amounts of organic waste, which goes to landfills every day, but also raised the application of chemical fertilizers in the soil to support increased food production. The fruits and vegetables processing industries (where biodegradable waste represents 25-30% of processed raw materials), generates significant amounts of waste which are in most cases, landfilled, representing unsustainable practice with environmental hazards. Recently the interest of many researchers have been raised in producing biochar from such bio-residues and using the obtained product as a soil amendment, due to the urgent need to find an alternative to chemical fertilizers. Fertilizers made of waste biomass available in abundant amounts, might promote global food production, enhance CO_2 capture, and reduce waste generated improving soil health and the overall environment.
Since the peaches (*Prunus persica* L.) have an important role in Serbia's fruit production with an average of five years of production approx. 45,000 t, which generates approx. 9,000 t peach stones waste (Statistical office of the Republic of Serbia, 2022), have been chosen as lignocellulosic biomass for biochar preparation. The specific aim of the present work was to investigate the characteristics of the waste peach stones biochar from the corner of its possible agriculture application in an environmentally sustainable manner.

Materials and Methods

Material: Peach stones were obtained from the Juice Factory Vino Župa Aleksandrovac, Serbia, where they have been classified as waste. They were washed, dried at room temperature, grinded by the vibrating disk mill Siebtechnik – TS250 (Siebtechnik GmbH, Germany), and sieved into a fraction between 0.1 to 0.5 mm (PS). Further, PS was pyrolysed at 500 °C under oxygen-limited conditions in a Nabertherm 1300 muffle furnace (Nabertherm, Germany) at the heating rate of 10 ºC min^{-1}, for 1 h. The obtained biochar (PS-B) was stored in containers with polypropylene caps in a dark place.
Methods: Scanning Electron Microscopy (SEM) analysis was performed under a vacuum, where samples were coated with gold and observed using a JEOL JSM-6610 LV model (JEOL Ltd., Japan). Mass yield (%) of PS-B was expressed as the unit weight of biochar to the unit weight of dry PS times 100. For elemental analysis (C, H, N and S) Vario-EL III; CHNS-O Elementar Analyzer (Hanau, Germany) has been used. Analysis of moisture, volatile matter (VM) and ash were performed according to the ASTM D1762-84 (2007) standard. Fixed carbon (FC) was calculated by subtracting the ash, moisture and VM content from 100. The determination of the mineral content was performed by using atomic adsorption spectrometers (Perkyn Elmer AAS Analyst 300). The value of the suspension pH (pH_{sus}) was determined according to ASTM D6851-02 standard: 0.2 g of samples were suspended in 30 cm^3 of distilled water, and left for 72 h with occasional stirring, after which suspension pH value was measured by using a pH meter SensION3 (Hach, USA). The point of zero charge (pH_{pzc}) values were determined by using a method described by Milonjić et al. (1975).

Results and discussion

The SEM micrographs of PS and PS-B (Fig. 1) revealed the changes after pyrolysis. It can be seen that the PS-B sample has a significantly higher surface area and porosity. It is evident also that PS-B contains larger (20-30 μm) and smaller (1-3 μm) diameter pores. The porosity is increased by forming the pores located inside the larger ones, compared to the raw sample. The formation of secondary pores indicates the release of volatile matter during this treatment (Peiris et al., 2019). Previously done BET analysis, (Lopičić et al., 2021) confirmed SEM analysis results: specific surface area (SSA) increased from 0.545 m^2g^{-1} (PS) to 159.1 m^2g^{-1} (PS-B) where PS-B has a highly developed micro- and meso- pore structures in comparison to PS. Increased surface area and biochar porosity are highly beneficial to soil water retention capacity.

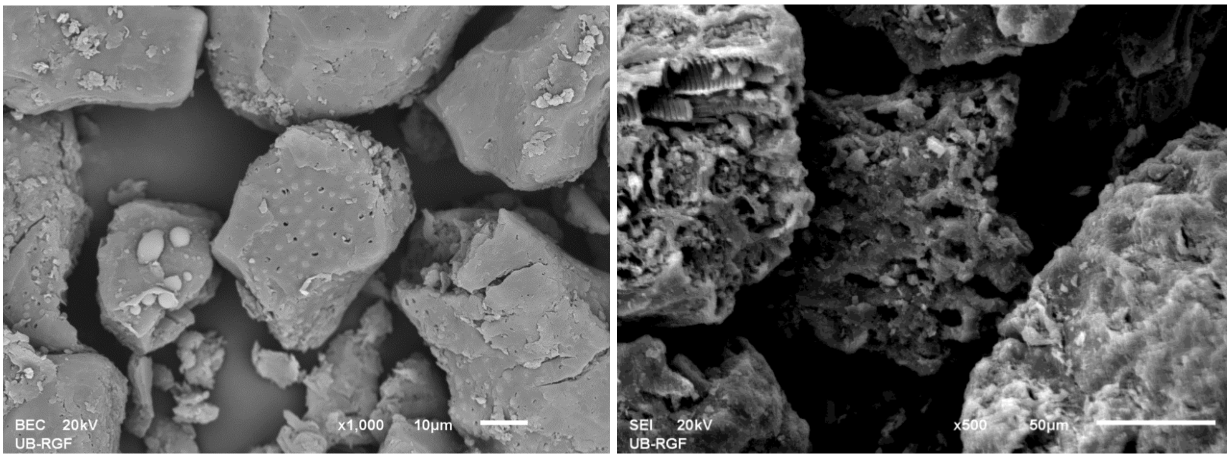

Figure 1. SEM micrographs of raw (PS) – left, and biochar sample (PS-B) - right

Such a larger surface area with a highly porous structure is suitable for absorbing soluble organic and inorganic nutrients and for providing a favourable environment for the growth of useful soil microbes. The advantages of biochar as a soil amendment are multiple. The presence of the microbes on biochar surface significantly increases microbial biomass carbon in soil compared with chemical fertilizers (Panwar et al., 2019). Another advantage of biochar as a soil amendment agent is carbon sequestration, which arises from the fact that biochar, is capable to absorb atmospheric carbon dioxide. According to Ahmad et al. (2014), the sorption of organic contaminants present in the soil depends mainly on surface area and pore size, thus biochar, in general, shows greater sorption capacity for organic than inorganic contaminants. However, ion exchange, electrostatic attraction and precipitation are dominant mechanisms for the remediation of inorganic pollutants by biochar.
Table 1 summarizes key parameters collected from the literature concerning biochar characteristics produced from different feedstock at pyrolysis temperature of 500 °C. In this table, the main physicochemical characteristics of biochar PS-B are also given. As can be seen, poultry manure and sewage sludge generate a higher biochar yield in comparison to agro residues and woody biomasses. This is related to the presence of inorganic components in feedstock, which is in accordance with relatively high ash content. However, high biochar yield can be achieved from agro waste too, if it has a high level of minerals and lignin (Sohi et al., 2010).

Table 1. Characteristics of biochars produced from different feedstock at pyrolysis temperature 500 °C

Feedstock	Yield*	VM*	FC*	Ash*	pH	C*	H*	O*	N*	Ref
Corn cobs	18.9	-	-	13.3	7.8	77.60	3.05	5.11	0.85	Mullen et al., 2010
Corn stover	17.0	-	-	32.8	7.2	57.29	2.86	5.45	1.47	
Orange peel	26.9	-	-	4.3		71.40	2.25	20.30	1.83	Chen & Chen, 2009
Pine needles	26.1	-	-	2.8	-	81.67	2.26	14.96	1.11	Chen et al., 2008
Rapeseed plant	35.6	17.5	69.6	12.9	-	75.03	2.62	7.79	1.41	Karaosmanoğlu et al. 2000
Poultry manure	72.0	7.3	68.6	24.0	11.0	51.56	1.87	40.32	5.50	Ahmad et al., 2014
Peach stone	28.14	25.20	71.89	0.73	5.76	69.37	2.74	27.49	0.30	This paper

*data reported in (Lopičić Z. et al., 2021)

Elemental composition and their calculated molar ratios are often used to reveal the temperature effects on the functional chemistry of biochars: an increase in pyrolysis temperature results in lower molar H/C and O/C ratios, thereby indicating dehydration and deoxygenation of the biomass (Ahmad et al., 2014). From Table 1 is evident that PS-B characteristics are in accordance with characteristics of biochar from a similar feedstock. The share of H and O decreased over C, leading to products with higher C concentration, due to the loss of biomass's volatile compounds during the process of pyrolysis. This can be seen by the high content of FC and low VM content. In addition, the value of H/C (0.04) and O/C (0.4) molar ratios indicate the stronger aromatic and stable structure of biochar, and the lower number of polar functional groups on the surface of PS-B (Lopičić et al., 2021). The values of these parameters are significant because they determine the stability of biochar in soil. According to Spokas (2014), who investigated the stability of biochar in soil, a lower O/C ratio results in more stable biochar. Accordingly, when the O/C molar ratio is > 0.6, biochar will possess a half-life of < 100 years; if the range is 0.2–0.6, the half-life range is 100 - 1000 years, and if the molar O/C ratio is less than 0.2, the half-life will be more than 1000 years (Spokas, 2014). Therefore, biochar remains in soil longer if the molar ratio of O/C in biochar is lower. Obtained results for PS-B indicate that its half-range in the soil will be more than 500 years.

The low ash content of 0.73% for the PS-B indicates that most of the biochar is made from the combustible phase. Nevertheless, the value of pH_{sus} of PS-B is higher (5.76) in comparison to raw PS (4.10). The reason for that can be found in feedstock composition (PS) and the number of present minerals in it, like potassium, magnesium and calcium ions. According to Lopičić (2017), the content of essential elements in the ash of PS are: calcium (4.2%), magnesium (6.99%) and potassium (25.4%), as well as phosphorus (26.88%). The analysis of major components of mineral matter in ashes of PS-B revealed that the K, Ca and Mg are major components of the ashes. The content of K was 19.9%, Mg was 9%, while the Ca content was also significant. The amount of Fe was approximately 2% for both samples, while the number of other components analysed was. This mineral composition is beneficial for promoting plant growth, suggesting that PS-B can be used in soil enrichment and approves that this material can be used as a supplement in agricultural practice.

The pH_{pzc} was also determined because it describes the acid-base sorbent behaviour at which the net surface charge of the sorbent becomes electrically neutral. The biochar surface charge has been significantly changed after pyrolysis by increasing the pH value of the point zero charge pH_{pzc} from 4.8 (PS) to 6.0 (PS-B). These results show the basic character of the PS-B. These results agree with the overall literature about biochars that typically indicate basic properties.

Conclusion

In this paper, peach stones, renewable, waste material, which is reutilized from landfills, were pyrolysed to obtain biochar (PS-B). In order to determine PS-B's potential as a soil amendment, its characterization has been performed. The pyrolysed sample contains a large multi-porous surface area, with increased aromaticity compared to the native sample. Biochar PS-B has the potential to remain in soil longer since the molar ratio of O/C in biochar is low (0.4). Mineral content and value of pH_{sus} also approve that can be used as a supplement in agricultural practice, while the value of pH_{pzc} shows a basic character of biochar PS-B indicating its potential to reduce the soil acidity. The results clearly indicate that PS-B has potential for soil improvement, which at the same time reduces the number of landfill wastes and decreases greenhouse gas emissions by carbon sequestering and reduction of methane emissions from landfills.

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