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PHYSICOCHEMICAL CHARACTERISATION OF VINE WASTE USED FOR PRODUCING BIOCHAR

Violeta Alexandra ION[1], Andrei MOȚ[1], Vlad Ioan POPA[1], Suzana CALCAN[2, 3], Liliana BĂDULESCU[1], Ionuț Ovidiu JERCA[1], Cornel BANIȚĂ[4], Oana Cristina PÂRVULESCU[2]

[1]Research Center for Studies of Food Quality and Agricultural Products, University of Agronomic Sciences and Veterinary Medicine of Bucharest, 59 Marasti Blvd, District 1, Bucharest, Romania
[2]Chemical and Biochemical Engineering Department, University Politehnica of Bucharest, 1-3 Gheorghe Polizu, Bucharest, Romania
[3]Scient Research Center for Instrumental Analysis, 1 Petre Ispirescu Str., Tancabesti, Ilfov, Romania
[4]Pietroasa-Istrita Research Station for Viticulture and Fruit Growing, Pietroasele-127470, Buzau, Romania

Corresponding author email: andrei.mot@qlab.usamv.ro

Abstract

Plant wastes are often burned, leading to air pollution and significant loss of potential soil nutrients. In order to mitigate these drawbacks, the waste can remain or be added to the soil, but this may increase crop diseases and also greenhouse gas (GHG) emissions (e.g., CO_2, CH_4, N_2O). Pyrolysis of vine waste is a promising and relevant technique, and the obtained biochar can be further used as a soil amender, can enhance soil C sequestration and water holding capacity, reduce GHG emissions and nutrient leaching, increase soil fertility, resulting in agronomic, environmental, and economic benefits. The aim of this study was to characterise vine waste from a physicochemical point of view in order to be used as raw material for producing biochar, which will be applied as soil amender. Plant waste material (grapevine prunings and marc) was received from Pietroasa-Istrita Research Station for Viticulture. The materials were characterised in terms of dry matter, loss on ignition, surface morphology, total carbon and nitrogen, bulk density, water holding capacity, pH, electrical conductivity, and mineral content. The obtained results indicate that grapevine prunings and marc are suitable materials for obtaining biochar.

***Key words**: biochar; grape marc; grapevine prunings; physicochemical characterisation.*

INTRODUCTION

Conversion of organic materials to biochar via pyrolysis provides an alternative to manage various wastes. Crop- and forestry-waste, vegetal and animal waste resulting from industrial processing, urban-yard waste, animal manure, organic fraction of household solid waste municipal sewage sludge have been widely used to obtain biochar (Kung et al., 2015; Purakayastha et al., 2019).

Waste valorisation by pyrolysis can have significant agronomic, environmental, and economic benefits. In addition to biochar, pyrolytic bio-oil and gases are produced by pyrolysis. They can be further upgraded to obtain fuels and different chemicals, enhancing the process efficiency (Ceatra et al., 2016). Pyrolysis can be slow, fast or flash, depending on the heating rate and residence time. Slow pyrolysis, also called conventional carbonization, produces biochar by heating biomass at a low heating rate (0.1-1°C/s) and relatively long residence time (up to several days) (Qian et al., 2015). Pyrolysis process is usually performed in the presence of an inert (nitrogen, argon) or oxidizing (steam, carbon dioxide) carrier gas (Dobre et al., 2010; 2012; Pârvulescu et al., 2016).

Biochar is a highly porous carbon-based material that has significant aromaticity and anti-decomposition capabilities (Wang et al., 2017). Biochar has a high potential as soil amender, to improve soil properties and its capacity for increasing nutrient retention (*i.e.*, decreasing nutrient leaching and gaseous nutrient emission), while also allowing nutrient release (Yang et al., 2017). Biochar can improve the physical and chemical characteristics of soil and promote crop yield (Schulz et al., 2013). Change in water holding capacity of soil by adding biochar is one of the key factors that can explain the crop growth (Karhua et al., 2011).

According to the International Organisation of Vine and Wine (https://www.oiv.int/), in Romania, in 2016, there were up to 191 356 ha of vineyards. Up to 20% of the harvested wine grape becomes waste during wine production. Grape marc can be used for compost and substrate in ornamental plants (Madjar et al., 2014a) and vegetables (Carmona et al., 2012), as well as for obtaining biofuel (Xu et al., 2009) and biochar (Ibn Ferjani et al., 2019). The use of vine pruning materials in pyrolysis processes solves several environmental problems, including managing large volumes of waste generated annually and reducing CO_2 emissions during uncontrolled waste burning (Nunes et al., 2021). The aim of this study was to characterise the wine waste from a physicochemical point of view, in order to be used as raw material for producing biochar, which will be further applied as soil amender.

MATERIALS AND METHODS

Biomass waste materials

Both grape marc and grapevine prunings came from Pietroasa-Istrita Research Station for Viticulture and Pomiculture, part of the University of Agronomic Sciences and Veterinary Medicine of Bucharest.

Grape marc came from Cabernet Sauvignon wine production. The wine was separated from the marc after 14 days of fermentation by draining. After separation, the marc was pressed to about 1.8 bar, using a pneumatic press, discharged and stored in plastic bags until it was shipped to the laboratory.

Grapevine prunings came from a viticulture area of 2.29 ha, cultivated with the Cabernet Sauvignon variety. The grapevine prunings were cut at the beginning of March 2021 and ropes with a diameter between 9-14 mm were selected from the fruit rings left after the cutting process was carried out.

In order to be further processed, both samples were analysed in terms of dry matter. After dry matter determination, grape marc was directly placed in an oven at 105°C until constant mass was achieved and then stored in a desiccator for further characterization. Grape prunings were cut at a length of 1-2 cm and further processed similar to grape marc.

Proximate and ultimate analysis

The determination of the dry matter (*DM*) was performed in a Memmert UN110 using the following steps: first step - 1 h at 70 °C, second step - at 105 °C until constant mass was achieved. The results were expressed as mass percentage.

Ash content (*AC*) was determined by ignition of 1 g of sample at 650°C for 6 h in an oven (Nabertherm, B150) until all carbon was removed. The final calculation was based on the percentage of ash from the original compound.

The volatile matter (*VM*) analysis method was based on ASTM D5142. 1 g of sample was weighed in a specific crucible with cover and placed in the oven (Nabertherm, B150). The furnace was heated (50°C/min) to a temperature of 950 ± 20°C and it was held for 7 min at this maximum temperature. *VM* was calculated with Eq. (1), where m_1 (g) is the mass of sample after drying in moisture test and m_2 (g) is mass of sample after heating in volatile matter test (Aller et al., 2017).

$$VM(\%) = \frac{m_1 - m_2}{m_1} \times 100 \quad (1)$$

Fixed carbon content (*FC*) was calculated based on the average obtained from three determinations of ash content and volatile matter. Fixed carbon content is the difference between 100 and the sum of the percentages of moisture, ash, and volatile matter. Since prior to analysis both samples were dried to constant mass, moisture was not taken into consideration.

For ultimate analysis of samples, an amount of 1-3 mg was used to determine the C, N, H, and S content. The analysis was performed using the CHNS elemental analyser (EuroVector EA3100 Elemental Analyzer), with cystine as standard reference material. Oxygen (O) was calculated by difference from the obtained results.

Mineral content

The mineral content was determined using Inductively Coupled Plasma - Mass Spectrometer (NexION 300S, PerkinElmer) for Co and Mo, and Inductively Coupled Plasma – Optical Emission Spectrometer (Optima 8300, PerkinElmer) for Ca, K, P, Mg, Fe, Al, Mn, Zn, B, and Cu. Briefly, 0.5 g of sample was mineralised with 5 mL of HNO_3 65 % and 0.5 mL of H_2O_2 30% using a Anton Paar PROSOLV microwave oven. After digestion, the samples were diluted to a final volume of 25 mL with ultrapure water and quantified based on an external calibration curve.

Physicochemical characterization

The dry bulk densities (*BD*) of the material were determined on the previously prepared samples, using cylinder method. The bulk densities were calculated using Eq. (2), where m_2 (g) is the mass of oven-dried sample within the cylinder, m_1 (g) the mass of the empty cylinder, and V (cm^3) the volume of the cylindrical core.

$$BD = \frac{m_2 - m_1}{V} \quad (2)$$

Electrical conductivity (*EC*) and pH of grape marc and grapevine prunings were determined by blending 0.5 g of milled sample with 20 mL of distilled water for 1 h using a magnetic homogenizer (IKA C-Mag HS7). *EC* and pH of the suspension were recorded using a Mettler Toledo SevenExcellence Multiparameter.

A Carl Zeiss EVO LS 15 scanning electron microscope, at accelerating voltages of 5 kV, 2001 Pa, and different magnifications was used in order to observe the morphology of the samples.

Measurement of water holding capacity (*WHC*) of plant material was performed as follows: around 20 g of each sample was introduced in a container with glass wire mesh at the bottom and the container was placed in a glass beaker with water for 24 h. The samples were then fixed in a larger recipient to let excessive water drain for 6 h. Wet sample was then weighed and oven-dried at 105 °C until no more weight (Bikbulatova et al., 2018). *WHC* was calculated using Eq. (3), where m_1 is the mass of glass container, m_2 the total mass of wet material and glass container, and m_3 the mass of oven-dried material sample and glass container.

$$WHC(\%) = \frac{m_2 - m_3}{m_2 - m_1} \times 100 \quad (3)$$

All experimental determinations were conducted in triplicate and the results were expressed as the mean values ± SD.

RESULTS AND DISCUSSIONS

Proximate and ultimate analysis

Both grape marc and grapevine prunings were conditioned prior characterization. Grape marc came with a dry mass content of 38.74 ± 4.94% compared to 82.80 ± 1.38% of grapevine prunings, therefore both were dried in an oven to a constant mass.

Proximate analysis offers primary information about biochar when it is used as a solid fuel, but can also offer information about the transformation of waste material into biochar. Grape marc had a higher content of ash compared to grapevine prunings, up to 5.2 times higher. Ash content can be correlated with a higher mineral content of the raw material (Figure 1). Volatile matter is the organic fraction of moisture-free biochar that can migrate into the soil and become a source of food for soil microbes (Zhu et al., 2017). Grapevine prunings had a higher volatile matter content (83.03 ± 3.34%) compared to grape marc (75.92 ± 3.15%), but part of this volatile matter can be lost in pyrolysis process resulting in a biochar with higher fixed carbon content. Grapevine prunings also had a higher fixed carbon content (14.98 ± 3.45%) compared to grape marc (13.81 ± 3.13%), as shown in Table 1. According to Sun et al. (2017), the content of volatile and fixed matter is higher in plant biomass, such as woody pruning wastes, compared to other types of materials (agricultural waste, aquatic waste, nutshells and fruit peel, livestock manure, and residual sludge).

Biochar prepared from crop residues and woody materials also has a higher carbon content than biochar prepared from other sources, *e.g.*, manure (Tomczyk et al., 2020). Spokas (2010) stated that biomass composition in terms of O/C molar ratio is between 0.6 and 1 depending on the main component type (*e.g.*, cellulose, hemicellulose, lignin, starch).

Table 1. Proximate and ultimate results of waste vegetal material

	Sample	
	Grape marc	**Grapevine prunings**
***DM* (%)**	38.74 ± 4.94	82.80 ± 1.38
***AC* (%)**	10.27 ± 0.04	1.99 ± 0.12
***VM* (%)**	75.92 ±3.15	83.03 ± 3.34
***FC* (%)**	13.81 ± 3.13	14.98 ± 3.45
C (%)	50.10 ± 0.57	48.39 ± 0.61
H (%)	6.30 ± 0.27	6.65 ± 0.28
N (%)	2.20 ± 0.27	0.49 ± 0.02
O (%)	41.40 ± 1.79	44.47 ± 0.85

In our case, the O/C molar ratio of grapevine prunings was slightly higher (0.69) than that of grape marc (0.62), but the final O/C molar ratio of biochar will largely depend on the pyrolysis conditions. According to Budai et al. (2013), biomass with high values of H/C and O/C ratios exhibits low resistance to degradation, hence these values should be taken in consideration when the material will be subjected to pyrolysis, to obtain a graphite-like biochar.

Mineral content

As expected, grape marc had a high content of K, N, and P compared to lignocellulosic material (grapevine prunings). Grape marc contains almost 11 times more K than grapevine prunings, as shown in Figure 1. P content was 0.34% in grape marc compared to 0.12% in grapevine prunings and also N content was higher in grape marc. Both N and P are volatile and can be lost during pyrolysis, depending on the operating temperature.

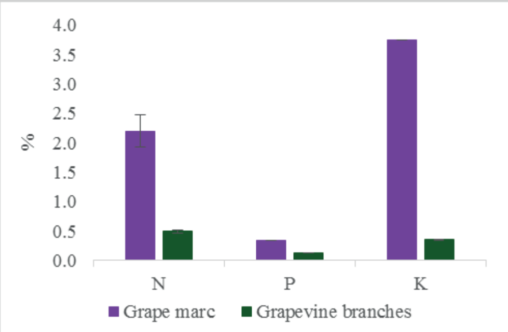

Figure 1. NPK results of waste vegetal material

Both samples were characterized in terms of content (mg/kg) of Ca, Mg, Fe, Al, Mn, Zn, B, Cu, Co, and Mo. Higher levels of mineral content were in grape marc samples (Table 2), except for Mg (1246.03 ± 29.76 mg/kg in grapevine prunings compared to 799.37 ± 3.39 mg/kg in grape marc). Grape marc had a total content of Ca of 5790.25 ± 2.85 mg/kg, higher than that of grapevine prunings (4799.20 ± 37.69 mg/kg). The large amount of calcium in the raw materials will be found in large proportion in the final product (biochar), which makes it suitable to be used as an amender for acid soils.

Grape marc also contains up to 12 times more Fe and up to 18 times more Al compared to grapevine prunings. Mineral content of the biomass feedstock can be correlated with the mineral content of biochar, taking into account that there are little losses of minerals during pyrolysis. Similar content of Mn was observed in both samples, *i.e.*, 26.87 ± 0.80 mg/kg for grape marc and 25.63 ± 0.02 mg/kg for grapevine prunings. Slightly differences were also observed in Zn content, *i.e.*, 13.79 ± 0.86 mg/kg for grape marc and 10.26 ± 0.00 mg/kg for grapevine prunings. Grape marc had higher content in B (45.58 ± 1.28 mg/kg), Cu (19.75± 0.37 mg/kg), Co (0.064 ± 0.001 mg/kg), and Mo (0.064 ± 0.001 mg/kg), compared to the content of B (4.74 ± 0.40 mg/kg), Cu (3.96 ± 0.01 mg/kg), Co (0.027 ± 0.000 mg/kg), and Mo (0.128 ± 0.001 mg/kg) in grapevine prunings.

Physicochemical characterization

Electrical conductivity (*EC*) of grape marc was more than 4 times higher than that of grapevine prunings. *EC* of grape marc was of 2.09 ± 0.05 dS/m compared to 0.50 ± 0.01 dS/m for grapevine prunings, with more plant-available nutrients (Madjar et al., 2014b). Higher levels of *EC* of grape marc are due to its higher values of nutritive element content.

Table 2. Mineral content in biomass waste material

	Sample	
	Grape marc	**Grapevine prunings**
Ca (mg/kg)	5790.25 ± 2.85	4799.20 ± 37.69
Mg (mg/kg)	799.37 ± 3.39	1246.03 ± 29.76
Fe (mg/kg)	148.89 ±4.14	12.72 ± 0.02
Al (mg/kg)	168.75 ± 2.59	9.38 ± 0.02
Mn (mg/kg)	26.87 ± 0.80	25.63 ± 0.02
Zn (mg/kg)	13.79 ± 0.86	10.26 ± 0.00
B (mg/kg)	45.58 ± 1.28	4.74 ± 0.40
Cu (mg/kg)	19.75± 0.37	3.96 ± 0.01
Co (mg/kg)	0.064 ± 0.001	0.027 ± 0.000
Mo (mg/kg)	0.213 ± 0.004	0.128 ± 0.001

Bulk density (*BD*) of raw material depends on the chemical composition, but also on the size and distribution of the particles. Grape marc had a higher density (0.36 ± 0.01 g/cm^3) than grapevine prunings (0.33 ± 0.01 g/cm^3), mainly due to sample preparation. Moreover, grape marc had a higher acidity (pH = 3.85 ± 0.01) compared to grapevine prunings (pH = 5.41 ± 0.53). During pyrolysis, the pH of the biochar increases with operating temperature (Yang et al., 2017), so the initial pH value of the grape marc and grapevine prunings is not highly significant in characterization of biochar.

SEM images shown in Figure 2 indicate a higher porosity of grapevine prunings, with pore diameters ranging from 40.46 µm to 120.7 µm at the center of the prunings and from 40.66 µm to 69.86 µm at the edge. For grape marc, it was difficult to determine surface porosity due to its complex mix (waste seeds, skin, and stalks). Grape marc has a higher water holding capacity (*WHC*), *i.e.*, 71.60 ± 3.43%, compared to 55.41 ± 1.43% for grapevine prunings.

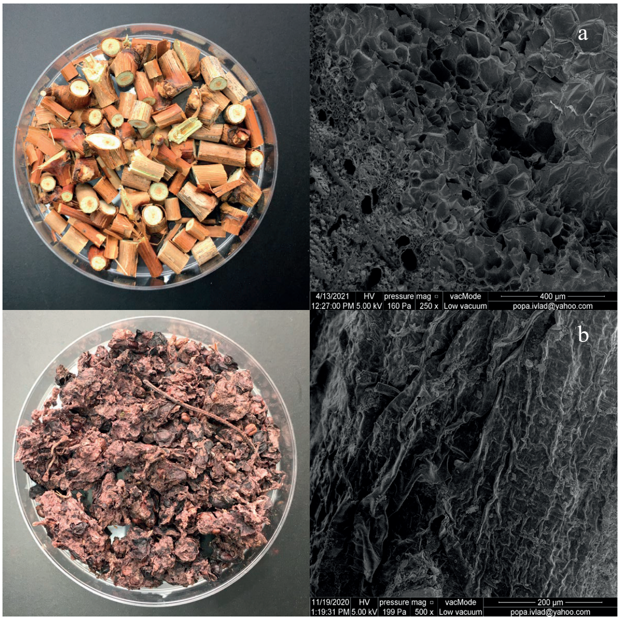

Figure 2. SEM analysis of vegetable waste material: (a) grapevine prunings and (b) grape marc

CONCLUSIONS

The properties of the biochar produced by pyrolysis can be significantly influenced by feedstock type, reactor design, pyrolysis temperature, and heating rate.

Characterisation of pyrolysis feedstock is essential to obtain a biochar applied for specific purposes. Several analytical techniques were used to characterise two types of biomass waste, *i.e.*, grape marc and grapevine prunings.

Proximate and ultimate analyses, SEM analysis, measurements of mineral content, pH, *EC*, *BD*, and *WHC* were performed. Both vegetal materials had high content of N, P, K, Ca, Mg and also micronutrients. A high content of C and nutrients as well as values of *WHC* over 50% suggest that grape marc and grapevine prunings are suitable for producing biochar which could be applied as soil amender.

Further analysis should be conducted to determine the available plant nutrients and their variation during pyrolysis.

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