Conversion of olive oil by-products into carbon rich chars using hydrothermal carbonisation process

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I. Introduction

The significant production of olive oil in the Mediterranean region is accompanied by the production of highly polluting by-products such as phenols, phytotoxic and antimicrobial substances (Aggoun et al. 2016), contained in olive mill wastewater (OMW) and olive solid waste (OSW). Their presence in the nature could cause significant deterioration to the ecosystem balance. Recent studies emphasized on the high content in nutrients of these wastes, thus opening new perspectives to their valorization in the agricultural field. Moreover, the obtained hydrochars can be potentially used in soil and water depollution processes. In the present work, a preliminary study on the transformation of OMW to carbon-rich chars is proposed. In order to enhance their physico-chemical properties, a thermal modification of these by-products has been performed by hydrothermal carbonization technique. The quality of the produced hydrochars was then analyzed by using complementary physico-chemical characterization techniques.

II. Materials and methods

Olive mill wastewater (OMW) was collected from a local olive mill plant in the Touta region (Tunisia) and stored in cans at low temperature (< 4°C). OMW was then filtered and dried at 60°C overnight to be used as feedstock without any pretreatment or purification. Hydrochars were prepared according to the experimental conditions cited in table 1. Generally, deionized water was added to the corresponding feedstock at a ratio of 1:9 (g of solid feedstock: mL of deionized water). The mixture was then placed in an autoclave with a capacity of 100 mL. Three different experimental temperatures were explored for the hydrothermal treatment: 180, 200 and 220°C. The produced hydrochars were named as Temperature (°C) / Feedstock / Time (h) accordingly to the preparation conditions. The heating gradient (10°C/min) and the residence time (24h) were maintained constant for all experiments. After carbonization, the suspensions were filtered to recover the solid residues so-called hydrochars.

Table 1: Experimental conditions for the hydrothermal carbonization of OMW

T°max (°C)	Feedstock	Time (h)	Code
180	OMW	24	180/ OMW /24
200	OMW	24	200/ OMW /24
220	OMW	24	220/ OMW /24

The characterizations of the produced hydrochars were performed by thermogravimetric analysis, scanning electron microscopy and Fourier transformation infrared spectroscopy.

III. Results and discussion

Firstly, the carbonization efficiency was obtained by measuring the mass yield of the different hydrochars. A significant difference between the quantity of produced hydrochars was observed in relation to the nature of the carbonized feedstock as well as of its content in minerals and fixed carbon. Results showed a decrease in the hydrochar yield when increasing the carbonization temperature, due to the increase of the volatile matter percentage. The highest carbonization yield of 30% was found for experiment 180/OMW/24, while the lowest (15%) for 220/OMW/24.

SEM images showed a similar morphology among the different produced hydrochars. The appearance of spherical shaped structures was clearly detected at carbonization temperatures of 180 and 200°C. According to Wang et al. (2018), the formation of these specific spherical aggregates could be attributed to the dehydration mechanism that occurred in the carbon structure of cellulose and lignin, accompanied with their depolymerization caused by the effect of the inner pressure.

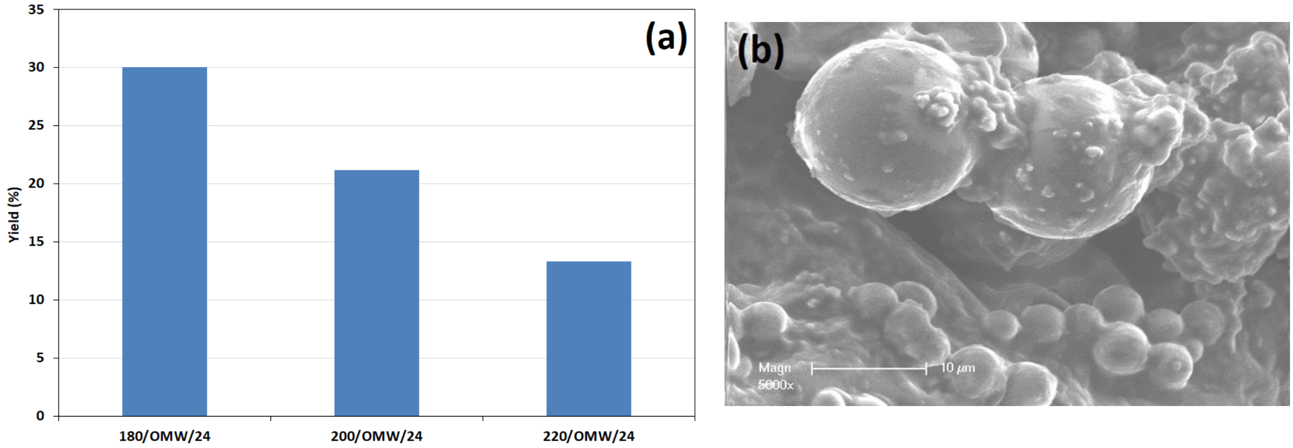

Figure 1: (a) Carbonization yield for the different experiments using OMW as feedstock and (b) SEM image of the 220/OMW/24 hydrochar

The carbonization of OMW increased the percentage of fixed carbon in the produced chars from 8% to 13% by increasing the temperature from 180 to 220°C, respectively, as showed by elemental analysis. It is worth to mention that a significant percentage of volatile matter was observed and estimated at 81%. The low concentration of OMW in minerals was translated in a decrease in the ash content when increasing the carbonization temperature.

The effect of the carbonization temperature on the chemical properties of the hydrochars surface was assessed using FTIR spectroscopy. The different specters related to the raw and carbonized OMW showed an important density of surface functional acidic (phenolic, carboxylic and lactonic) and basic (hydroxyl) groups. The increase of the carbonization temperature caused the appearance of a peak related to the vibration of the aromatic (719 cm^{-1}) and nitrile (1161 cm^{-1}) groups, while the band related to –C–H aliphatic peaks disappeared (1645 cm^{-1}). Moreover, a vibration of +35 cm^{-1} was recorded between the FTIR specters of OMW and 220/OMW/24 at the peak related to carboxylic (1743 cm^{-1}) groups. This could be assigned to a decarboxylation mechanism occurring during the hydrothermal treatment. Hydroxyl groups were less affected by the carbonization temperature of OMW.

IV. Conclusion

In this study, olive mill waste issued from the olive oil production were thermally modified using hydrothermal carbonization technique at different temperatures. Rising the treatment temperature affected significantly the cellulosic matrix of the hydrochars, leading to the production of a thermodynamically less stable carbon structure with amorphous features. The thermogravimetric analysis of the produced hydrochars showed a significant change in their elemental composition depending on the feedstock source. OMW presented a content in volatile matter that exceeded 80%. This observation emphasizes on the necessity of impregnating OMW on a carbon-rich matrix in order to increase its stability and reduce the amount of volatile matter at high carbonization temperatures. Finally, the FTIR analysis showed a high concentration of both acid and basic groups that could be of great importance in case of use as adsorbent in liquid or gas media. Further investigations are currently taken to increase the physio-chemical properties of the produced chars and their application in agricultural and environmental purposes.

Reference

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