Production of biochar from olive mill solid wastes for the removal of heavy metals from contaminated industrial wastewater

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Production of olive oil is considered as one of the most important economic agro-food sectors in the Mediterranean basin. The traditional oil industry generates two byproducts at the end of the process, olive mill solid waste (OMSW) and olive mill wastewater (OMW), which are well known as environmental pollution problems with very low economic value. Crude OMSW, the leftover solids is a mixture of skin, pulp, and seeds that can potentially serve as a source for heat, bioethanol production and compost. It comprises approximately 35% of the olive fruit weight, is rich in carbohydrates, and is available in appreciable quantities in the Mediterranean region. Global annual production of OMSW has been estimated to approach ca 4×10^8 Kg dry matter. The OMSW is consisted mainly of cellulose, hemi cellulosic and lignin with percentage ranges of 38-50%, 23-32% and 15-25% respectively. Thermochemical conversion of lignocellulosic biomass has been considered as a viable option to produce intermediate liquid streams for biofuels and biochemical such as biochar; in addition lignocellulose of OMSW is used to produce bioethanol (Abu Tayeh *et al*, 2014, 2016). During the conversion process, biochar is generated as a byproduct of pyrolysis; its optimization and application is essential to make the overall process economically feasible. The complex and heterogeneous chemical and physical composition of biochar provides an excellent platform for its use in removal of contaminants through sorption. We offer to test the use of OMSW as feedstock for biochar.

The main objective of the current study was to produce biochar to be used for removing different contaminants from industrial wastewater such as heavy metals (HMs) and Poly-aromatic hydrocarbons (PAHs). The results showed that the yields of biochar produced through pyrolysis of OMSW from "Picual" and "Suri" olive cultivars at 450^0C were in average ca 25% (Table 1.

Table 1. Yield of biochar production at different pyrolysis temperature. Each data point represents average of 3 replicates ± SD.

	Picual			**Suri**		
Temperature	250^0C	350^0C	450^0C	250^0C	350^0C	450^0C
Yield %	55.71	35.37	25.7	54.65	31.47	23.96
± SD	0.935	0.45	0.63	0.459	0.245	1.1

The calculated surface area of the produced biochar was 1.65 and 4.3 m^2/g for "Picual" and "Suri", respectively and 1100 m^2/g for activated carbon. The results showed that the accumulated adsorption (%) values of the "Picual" OMSW biochar (obtained at 450^0C) to the six heavy metals after incubation for 60 min was the highest compared to commercial activated carbon and the Suri cultivar (Figure 1). The removal capacity is mainly based on precipitation and adsorption mechanism as we can see the results of the biochar produced from "Picual" cultivar (Figure 2), and in addition depends on cultivar of the olives (data not shown).

Our results indicate that biochar produced from OMSW has high potential for removing heavy metals from solutions. The removal capacity depends on olive cultivar, temperature of biochar production, and pH of the solution. ATR-FTIR measurements show that in both "Suri" and "Picual" varieties C=O band ascribed to hemicellulose (at app. 1730 cm^{-1}) decreases by about 80% at 250^0C and disappears completely at 350^0C. Lignin rings bands (at app. 1590 cm^{-1}) also show similarity for both varieties. However, differences can be observed for the lignin deformation bands at 1420-1470 cm^{-1}: whereas for the "Suri" decrease was by 60%, 95% and 100% at 250, 350 and 450^0C, respectively. In the "Picual" samples it was 50%, 70% and 95% at 250, 350 and 450^0C, respectively, indicating that more lignin remains in the latter. The most significant difference was that at 250^0C an anionic carboxylic group forms at the "Picual" variety, as it is testified by a very sharp and strong peak at 1560 cm^{-1}. We confirmed the presence of this absorption bands in several samples. No indication whatsoever to such anionic group was noticed at the "Suri" samples.

Figure1. The accumulated adsorption (%) values of the different OMSW biochar types (obtained at 450^0C) to the six heavy metals after incubation for 0, 5,15,30,60 min. Each data point represents average of 3 replicates + SD.

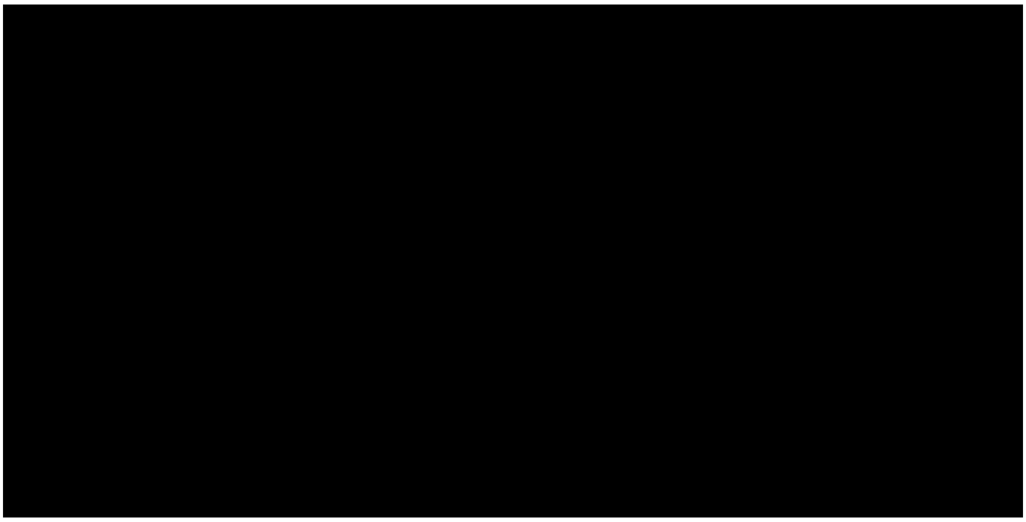

Figure 2. The accumulated concentration (%) values of the six heavy metals on "Picual" biochar obtained at 450^0C after incubation for 0, 5,15,30,60 min. Each data point represents average of 3 replicates + SD.

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