Production of biochar and activated biochar from olive mill solid waste for the removal of heavy metals and calcium from water

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Heavy metals (HMs) are major environmental pollutants, accumulated through the food chain to reach human consumers. Some of the metals are very toxic even at very low concentrations and are considered carcinogenic. Various technologies, either physical or chemical process, exist to treat and remove HMs from different industrial waste water, among them precipitation, ion exchange, membrane filtration, etc. However, some of these technologies have high operating and equipment costs, use of chemicals, and are of low effectiveness.

In the Mediterranean region, olive mill solid waste (OMSW) could serve as a cheap source of biomass for decontaminating wastewater and removal of calcium from water. The annual global production of OMSW has been estimated at 4×10^8 kg dry matter. Currently, OMSW is mostly disposed in the fields and could constitute a serious environmental problem due to its phytotoxic nature although its use as feedstock for bioethanol production was recently demonstrated (Abu Tayeh et al., 2016).

The research objective was to produce biochar from low OMSW using pyrolysis process to be used for adsorption and removing of HMs from industrial wastewater. The pyrolytic production of OMSW biochar at low temperatures was evaluated. We tested OMSW obtained from the two different olive cultivars (Picual and Souri), two oil production processes (two-phases vs three-phases) and two relatively low temperatures (350°C and 450°C) to evaluate for cheaper biochar production and lower mass loss. The study included two parts, pyrolysis, and then OMSW activation. In each part, the adsorption capacity was compared between different types of biochar. The results showed that biochar yield was 24-35% of the biomass; it was depending on pyrolysis temperature (as it increases the yield decrease). The surface area ranged between 1.65 - 8.12 m^2/g, as compared to 1100 m^2/g for commercial activated carbon (CAC) (Table 1). Following physical activation of the biochar using a physical process, the surface area of the Suri and the Picual biochar from two- as well as three- phase was increased by several folds (Table 1) (Abdelhadi et al., 2017). The porosity of the activated biochar was ranged between 87-91% (Table 1).

Table 1: Mean surface area of biochar produced at 450^0C of different whole OMSW types using BET models, and surface area and porosity of the activated biochar. Data is mean of 3 replicates ± SD.

Type: pyrolyzed at 450^0C for 5h	SA_{BET}(m^2/g) before activation	SA_{BET}(m^2/g) after activation	Porosity (%) after activation
Picual 2-phases	1.7 ± 0.01	501.5 ± 2.50	87.4
Picual 3-phases	8.13 ± 0.20	304.46 ± 1.52	91.5
Souri 2-phases	5.19 ± 0.19	213.27 ± 1.06	88.3
Souri 3-phases	5.3 ± 0.03	172.6 ± 0.86	91.1
CAC	1100 ± 5.50	-	-

The removal capacity of the **Picual two- phases biochar** obtained at 350^{0}C or 450^{0}C separated to cellulose and kernel compared to whole after incubation for 5 min with the 6 HMs are summarized in Fig. 1. The removal capacity of biochar was the heighest to Cu and Pb and ranged between 28-99% and the lowest was for Se which maximum reached 26%. Biochar produced at 350^{0}C was with better capacity to remove HMs compared to 450^{0}C. Therefore, it is better to use pyrolysis process at 350^{0}C to produce biochar for HMs removal, where the yield is heigh and less energy is applied for the production process.The produced biochar showed very good HMs removal capacity, comparable and even better to that of CAC (data not shown). Interestingly, HMs removal capacity did not correlate with surface area, suggesting better methods of testing biochar production should be thought after. The removal capacity for the HMs was depended on the olive cultivar and processing type (data not shown). Picual cellulose of the two-phases pyrolysed at 350^{0}C showed the best cumulative removal capacity for HMs compared to the other OMSW types.

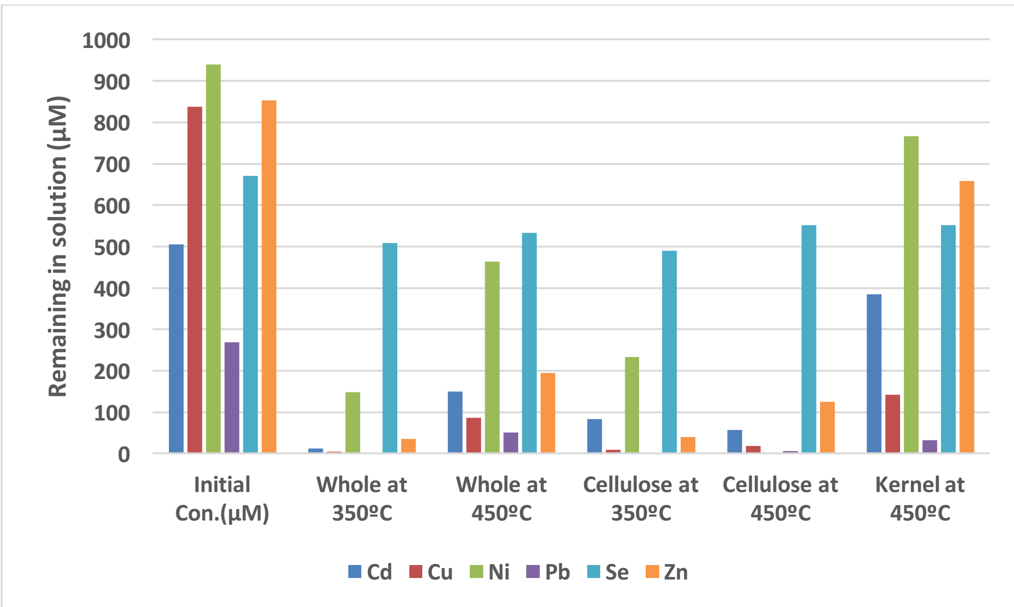

Figure 1: The remaining concentration (µM) of the six heavy metals using the **Picual two- phases biochar** obtained at 350^{0}C or 450^{0}C separated to Cellulose and Kernel compared to whole after incubation for 5 min. Data is mean of 3 replicates $\pm$ SD.

FTIR analysis indicated that the most significant absorption bands for the two-phases samples are peaks of (C-H) and (C-O) which are considerably smaller in the three-phases types. The main functional groups in metals removal are related to remains of cellulose in the produced biochar. We conclude that the removal of HMs is mainly depended on the cultivar type and the process used for oil extraction where Picual two- phases is better than the three- phases and similar trend was found in Souri types.

Physical and chemical activation of the OMSW biochar resulted in increase in the surface area, and preliminary results showed that the activated biochar was better in the removal of calcium where its capacity was 50-60% removal of the initial concentrations in the range of 50-100 ppm. Studies still running to find the best activation process to produce the best activated biochar for the removal of calcium from water.

References

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