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Production of biochar from olive mill solid waste for heavy metal removal

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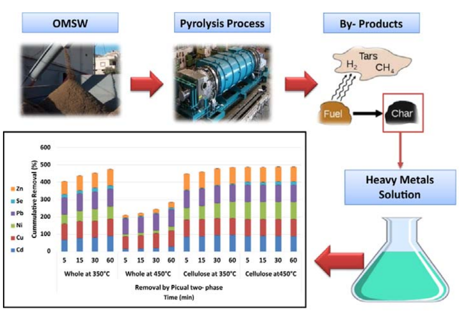
GRAPHICAL ABSTRACT



Biochar production from olive mill solid wastes for heavy metal removal

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ABSTRACT

Commercial activated carbon (CAC) and biochar are useful adsorbents for removing heavy metals (HM) from water, but their production is costly. Biochar production from olive solid waste from two olive cultivars (Picual and Souri) and two oil production process (two- or three-phase) and two temperatures (350 and 450 °C) was tested. The biochar yield was 24–35% of the biomass, with a surface area of 1.65–8.12 $m^2\,g^{-1}$, as compared to 1100 $m^2\,g^{-1}$ for CAC. Picual residue from the two-phase milling technique, pyrolysed at 350 °C, had the best cumulative removal capacity for Cu^{+2}, Pb^{+2}, Cd^{+2}, Ni^{+2} and Zn^{+2} with more than 85% compared to other biochar types and CAC. These results suggest that surface area cannot be used as a sole predictor of HM removal capacity. FTIR analysis revealed the presence of different functional groups in the different biochar types, which may be related to the differences in absorbing capacities.

1. Introduction

Heavy metals (HM) are major environmental pollutants, accumulating through the food chain to reach human consumers. Some of the metals are very toxic even at very low concentrations (e.g. lead and cadmium) and are considered carcinogenic (Jaramillo et al., 2009). Heavy metal pollution can originate from industrial activities such as electrolytic treatments, processing of plastic, metal and pigments, mining and disposal of batteries (Cd and Ni) and other consumer electronics (Blazquez et al., 2005, 2010). This discharge of heavy

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metals can affect the atmosphere, surface water, groundwater and oceans causing toxic effects upon entering the food chain (Jaramillo et al., 2009; Blazquez et al., 2005, 2010).

Various technologies exist to treat HM, among them precipitation, ion exchange, membrane filtration, reverse osmosis, evaporative recovery, coagulation, solvent extraction, reduction electrolysis and adsorption by charcoal and activated carbon (Baccar et al., 2009; Blazquez et al., 2005, 2010; Jaramillo et al., 2009; Martinez et al., 2009). However, these technologies have high operating and equipment costs, use chemicals, and are of low effectiveness when the contaminants are at low concentrations (Baccar et al., 2009; Blazquez et al., 2005, 2010; Martinez et al., 2009). Indeed, some of the procedures did not meet the Environmental Protection Agency (EPA) standards. Considering these limitations for utilizing low cost agricultural residues as feedstock for production of absorbants can be an economically alternative solution (Baccar et al., 2009; Martinez et al., 2009; Zabaniotou et al., 2008).

The use of carbonaceous materials such as coal, wood and coconut shell as feedstock for industrial production of biochar is expensive, especially since these materials are often imported. There is a need for cheap and locally available feedstock for the production of charcoal (Baccar et al., 2009). In the Mediterranean region olive mill solid waste (OMSW) could serve as a cheap source of feedstock for decontaminating industrial wastewater (Baccar et al., 2009).

Olive trees cultivation and oil production is a highly significant agricultural activity in the Mediterranean basin (Blazquez et al., 2010; Stavropoulos and Zabaniotou, 2005; Zabaniotou et al., 2008), with olive oil production increasing at a rate of 3.5–4% per year. There are two industrial scale methods for oil extraction from olive fruits: the traditional three-phase decanter system, which generates three different products: olive oil, olive mill wastewater (OMWW) and olive mill solid waste (OMSW), and the more modern two-phase centrifugation system which generates two products – olive oil and "pomace" which is a mixture of OMSW and OMWW (Blazquez et al., 2010). The annual global production of OMSW has been estimated at 4×10^8 kg dry matter, OMSW being a mixture of skin, pulp, and seeds and consisting mainly of cellulose (38–50% w/w), hemi cellulose (23–32%) and lignin (15–25%). Currently, OMSW is disposed in the field and could constitute a serious environmental problem due to its phytotoxic nature (Zabaniotou et al., 2008; Blazquez et al., 2010) although it's use as feedstock for bioethanol production was recently demonstrated (Abu Tayeh et al., 2014, 2016). OMSW has also been used to feed boilers and home fire places but these applications are not common due to the strong smell from its burning. Using OMSW as feed was also suggested, but its low digestibility makes it of low feed value (Shabtay et al., 2009). Production of charcoal through pyrolysis was also suggested (Aljundi and Jarrah, 2008). In addition, the OMSW has the potential to restore degraded soil, increase crop yield, fix carbon dioxide and remove contaminants from industrial waste water such as HM (Manya et al., 2014; Martinez et al., 2009; Tan et al., 2014; Zabaniotou et al., 2008).

Low cost biochar has been produced by pyrolysis of agricultural wastes such as fruit pits, sugarcane bassage, and nut shells (Zabaniotou et al., 2008; Jaramillo et al., 2009). Attention is increasingly focused on converting the abundant biomass of OMSW to a value-added product such as charcoal through pyrolysis (Aljundi and Jarrah, 2008). During pyrolysis, material is combusted under an inert atmosphere, usually at temperature between 400 and 800 °C. Unlike combustion, pyrolysis does not lead to air emissions, but optimization of pyrolysis is essential to make the method economically feasible and environmentally attractive (Aljundi and Jarrah, 2008; Park et al., 2013; Zabaniotou et al., 2008). The physical and chemical properties of biochar depend on the characteristics of the feedstock source and on the pyrolysis conditions, with temperature playing a key role (Tan et al., 2014). Biochar yield decreases as the peak temperature increases (Manya et al., 2014), but higher temperatures resulting in more effective microstructure develops. The chemical composition, pH, surface charge and thermal stability of biochar, as well as the HM fate in the biochar body are also functions of the pyrolysis temperature (Tan et al., 2014).

Table 1
The obtained mean yield (%) of biochar of the different OMSW types at 350 °C and 450 °C. Data is mean of 3 replicates ± SD.

Olive cultivar	Process type	OMSW component	Pyrolysis temperature (°C)	Yield (% w/w)
Picual	Two-phase	Whole[a]	450	25.69 ± 0.63
			350	35.37 ± 0.45
		Pulp	450	24.38 ± 0.67
			350	34.38 ± 0.56
		Kernels	450	26.79 ± 0.15
	Three-phase	Whole	450	25.01 ± 0.19
			350	33.4 ± 0.06
		Pulp	450	24.16 ± 0.41
			350	31.13 ± 0.06
		Kernels	450	26.71 ± 0.11
Souri	Two-phase	Whole	450	26.34 ± 0.14
			350	30.97 ± 0.08
		Pulp	450	23.62 ± 0.91
			350	30.37 ± 0.28
		Kernels	450	27.33 ± 0.37
	Three-phase	Whole	450	23.96 ± 1.08
			350	31.47 ± 0.24
		Pulp	450	23.91 ± 0.4
			350	31.53 ± 0.24
		Kernels	450	26.95 ± 0.41

[a] OMSW not separated.

Table 2
The mean surface area of biochar produced at 450 °C of the different whole OMSW types using Langmuir (MB) and BET methods. Data is mean of 3 replicates ± SD.

SA_{BET} ($m^2 g^{-1}$)	SA_{MB} ($m^2 g^{-1}$)	Type at 450 °C
1.0 ± 0.005	1.65 ± 0.14	Picual Two-phase
3.5 ± 0.018	8.12 ± 0.85	Picual Three-phase
1.2 ± 0.006	3.48 ± 0.01	Souri Two-phase
5.3 ± 0.027	4.30 ± 1.22	Souri Three-phase
1100 ± 5.5	–	Commercial activated carbon

OMSW have been shown to remove HMs contaminants from industrial waste water (Manya et al., 2014; Martinez et al., 2009; Tan et al., 2014; Zabaniotou et al., 2008), even without pyrolysis, with Cu and Ni adsorption capacity of 3.6 and 1.7 mg g^{-1}, respectively (Chouchene et al., 2014). Biosorbents derived as residues or by-products from the olive production were highly efficient at the pH range of 5–6 in the removal of Pb followed by Cd, but less efficient in the removal of Cu, Cr, Zn and particularly Ni (Anastopoulos et al., 2015).

In the current work, the pyrolytic production of OMSW biochar at low temperatures was evaluated. Given the importance of biomass type and pyrolysis temperature we tested OMSW from two different olive cultivars (Picual and Souri), two oil production processes (two-phase vs three-phase) and two relatively low temperatures (350 °C and 450 °C) to allow for cheaper production and lower mass loss.

2. Materials and methods

OMSW of Picual and Souri cultivars were collected during the winters of 2015 and 2016 from two- and three-phase production sites at Kibutz Ramon, Iksal, Tzipori and Daliat el Carmel, Israel. All samples were dried in the shade for two weeks then stored in plastic bags at room temperature (20–22 °C).

2.1. Preparation of biochar

The biochar was prepared from the two cultivars where each type was milled and used as mixed biomass (Whole) or physically separated