

# Novel Integrated Biorefinery for Olive Mill Waste Management: Utilization of Secondary Waste for Water Treatment

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**(5)** Supporting Information

**ABSTRACT:** Olive mill waste (OMW) management has been a problem in the Mediterranean basin for thousands of years. The solid exiting the extraction process contains polyphenols that are beneficial to humans and phytotoxic to plants. We propose an integrated biorefinery concept for OMW management: supercritical fluid extraction to recover polyphenols, followed by pyrolysis of the solid to produce bio-renewable fuels, and finally activation of the biochar to yield high surface area adsorbents for heavy-metals removal from water. This work details the impact of supercritical fluid extraction on biochars that are subsequently activated with CO<sub>2</sub> and KOH. Specific surface areas of the OMW biochars were over 2300 m<sup>2</sup>/g. Though supercritical fluid extraction increased the surface areas of raw, pyrolyzed, and KOH-activated OMW,



the effect was reversed for biochars activated using high-temperature  $CO_2$ . FTIR analysis showed that the supercritical fluid extraction significantly altered the surface functional groups of raw waste, but that activation conditions dictate surface characteristics of the resulting activated biochar. High-temperature KOH and low-temperature  $CO_2$  activation yielded activated biochars with the highest relative amounts of oxygenated functional groups. Activated samples demonstrate adsorption capacities upward of 400 mg of metal (Cd, Co, Cu, and Zn) per gram of sample and follow pseudo-second-order kinetics, with 75% adsorption capacity reached in less than 5 min. This integrated biorefinery concept simultaneously mitigates the environmental impacts of OMW disposal, yields high-value biopharmaceuticals and renewable energy, and provides a sorbent material for water treatment.

KEYWORDS: Olive mill waste, Supercritical fluid extraction, Waste mitigation, Activated carbon, Metal adsorption, Water treatment

# INTRODUCTION

To produce almost 3 million metric tons of olive oil in 2012–2013, over 12 million metric tons of waste was generated.<sup>1</sup> Given the short production time and relatively small cultivation area—over 95% of all olive oil is produced in the Mediterranean basin and Middle East—olive mill waste (OMW) represents one of the largest, most burdensome waste streams in the Mediterranean.<sup>2</sup> Most olive mills use a three-phase centrifugation system resulting in a large quantity of wastewater, high in antimicrobial activity,<sup>3</sup> and a solid waste stream, known as pomace (referred to here as OMW).<sup>4</sup> While polyphenols naturally present in olive oil may impart a variety of health benefits,<sup>5–7</sup> these same polyphenols make the disposal and treatment of OMW and wastewater difficult due to their

phytotoxic and bacteriostatic nature.<sup>8</sup> The biophenols present in OMW (including hydroxytyrosol, tyrosol, caffeic acid, rutin, and luteolin) vary in concentration from 0.02 to 10 g/kg, depending on species, season, and geography.<sup>9</sup> When substantial quantities of OMW are spread across agricultural land, the presence of these biophenols may be harmful to crops and soil microflora.<sup>10</sup> The purpose of our larger investigation is to shed light on possible disposal alternatives to the combustion, lagooning, or agricultural application of potentially phytotoxic solid OMW residue, to create a series of high-value byproducts. Extracting both energy and high-value products

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from waste materials further "greens" the biorefinery, replacing multiple uses of fossil fuels with biomass-based sources.<sup>11</sup>

Recently, we presented an integrated biorefinery concept for OMW, whereby we proposed to extract the naturally high concentration of polyphenols as well as valuable polyunsaturated fatty acids ( $\omega 3/\omega 6$ ) present in OMW using supercritical CO<sub>2</sub> extraction with ethanol co-solvent, and transform the remaining solid biomass via thermochemical conversion to energy and high surface area biochars (Figure 1).<sup>12</sup> We demonstrated that there is no energy penalty for the



**Figure 1.** Integrated biorefinery concept for extraction of polyphenols from OMW followed by energy and biochar recovery (dotted boxes indicate potential byproduct/energy recovery).

conversion of supercritical  $CO_2$ -extracted OMW versus raw OMW into bio-oil from pyrolysis; such bio-oil has similar characteristics to petroleum counterparts.<sup>13</sup> More importantly, we found that pyrolyzed samples had specific surface areas greater than 400 m<sup>2</sup>/g<sub>carbon</sub> prior to activation. The present work demonstrates the potential for OMW activated biochars (activated carbons (ACs) produced from biomass) resulting from the pyrolysis and activation of supercritical carbon dioxide (SCO<sub>2</sub>)-extracted OMW to treat metal-contaminated wastewater.

Activated carbons can be used for a variety of applications, including removal of heavy metals from wastewater streams via ion exchange<sup>14,15</sup> and dye removal from process water.<sup>16–20</sup> However, as Luo et al. note, we must find new resources for efficient, environmentally friendly adsorbents for removing heavy-metal ions from water,<sup>22</sup> as many of today's ACs are fossil-fuel-based. Biomass-based ACs can remove pesticides, pharmaceuticals, and endocrine-disrupting compounds from water.<sup>21–25</sup> Another potential application for such materials is in the construction of low-cost electrode surfaces in bio-electrochemical systems, where AC is a promising substitute for platinum-based catalysts for oxygen reduction and an electrochemically active coating for bio-electrodes.<sup>26</sup>

Pyrolysis, or heating in the absence of oxygen, results in the production of bio-oil, pyrolysis gas, and a carbonaceous char from biomass. The processing conditions (temperature, residence time, particle size) dictate the quantity and quality of products. There is a broad literature on the pyrolysis of raw OMW and OMW mixed with other waste products.<sup>27–32</sup> A large portion of the literature focuses on the potential for fabrication of bio-based ACs with high specific surface areas—

upward of 1000 m<sup>2</sup>/gram—via physical activation of carbonized OMW.<sup>33</sup> To the best of our knowledge, there have been no studies on bio-based ACs from OMW pyrolysis following SCO<sub>2</sub> extraction of the polyphenols. Moreover, there is no literature available concerning the performance of SCO<sub>2</sub>-extracted activated OMW biochars for the adsorption of contaminants from water.

Key components of the proposed integrated biorefinery concept include recovery of high-value biochemicals, followed by energy recovery, and finally by transformation of the remaining solid waste to bio-based ACs for water treatment, resulting in a process with zero solid waste. In the current work, we present findings on the ability to create activated OMW biochars for heavy metal and dye adsorption from wastewater, thereby converting the solid residue left after extraction of polyphenols and bio-oils to a byproduct for environmental treatment. Such transformations of low-value side products into value-added materials are imperative to the economic and environmental success of today's industries.<sup>34</sup>

# EXPERIMENTAL SECTION

**Olive Mill Waste.** OMW was obtained from an olive oil production plant in Calabria, Italy. The polyphenolic extraction was performed using supercritical fluid extraction as previously described.<sup>12</sup> Briefly, raw samples (OMW) were extracted with either pure supercritical  $CO_2$  (SCO<sub>2</sub>) or supercritical  $CO_2$  with ethanol as a co-solvent (SCO<sub>2</sub>+EtOH). Both extractions proceeded at a total pressure of 250 bar and 70 °C, with a  $CO_2$  flow rate of 80 kg/h. The raw OMW load was 7300 g for the SCO<sub>2</sub> run, and 7260 g for the SCO<sub>2</sub>+EtOH run, with 1500 g of ethanol. The co-solvent was used to increase the extraction efficiency of the polyphenols and polyunsaturated fatty acids as base for high-value nutraceutical products; though methanol is a better solvent in terms of partitioning of polyphenols, ethanol is preferred for downstream human consumption of the extracted compounds.<sup>35</sup>

**Preparation of OMW Biochars.** The OMW raw, SCO<sub>2</sub>, and SCO<sub>2</sub>+EtOH samples were ground in a ball mill and mechanically sieved to yield particles less than 125  $\mu$ m in diameter. The biochars were prepared by pyrolyzing raw and extracted OMW samples in an inert nitrogen environment (50 mL/min flow rate) in a 1-in. tube furnace. Approximately 5 g of each sample was loaded into a porcelain boat and inserted into the quartz tube. The OMW samples were heated under nitrogen to 110 °C and held at that temperature for 1 h to remove residual moisture. The samples were then heated at a rate of 20 °C/min to 600 °C and held for 30 min to produce the desired char. The OMW chars were physically activated in a CO<sub>2</sub> atmosphere (50 mL/min flow rate) at either 600 or 800 °C for 40 min, and a third set at 800 °C for 120 min. Activation was carried out at a heating rate of 10 °C/min in the tube furnace.

Chemically activated OMW samples were made in one step directly from the raw biomass. Solid potassium hydroxide (KOH) was used as the chemical activation agent in a ratio of 2:1 KOH:biomass. The KOH was dissolved in deionized water (weight ratio of 14:1 H<sub>2</sub>O to KOH), which was then mixed with the raw biomass samples in glass vials using a vortex mixer for approximately 5 min. The KOH-samples were soaked overnight (12-14 h) and then filtered. The solid was dried, uncovered, in a laboratory oven at 110 °C. Samples were then transferred to porcelain boats and activated in the tube furnace under nitrogen at either 600 or 800 °C at a ramp rate of 10 °C/min with a 30 min hold time. Once cooled, the samples were mixed with the same amount of deionized water used to dissolve the KOH previously in a 14:1 weight ratio of KOH to H<sub>2</sub>O and then neutralized with 1.2 M HCl, and subsequently dried overnight in a 110 °C laboratory oven. These dried activated samples were washed with deionized water to remove any salt that had crystallized, and then filtered. The chemically activated solid collected in the filter was dried, uncovered, in the oven overnight at 110 °C.

Table 1. Carbon Cont	ents and Surface Areas	of Untreated, Pyre	olyzed, and Activat	ed OMW Samples	with Particle	Sizes Less
than 125µm				-		

activation technique	sample $d_{\rm p}$ < 125 $\mu$ m	carbon content (mass fraction)	BET surface area $(m^2/g_{sample})$	specific BET surface area $(m^2/g_{carbon})$
untreated	raw OMW	0.85	2.47	2.91
untreated	SCO <sub>2</sub>	0.87	2.48	2.85
untreated	SCO <sub>2</sub> +EtOH	0.86	2.62	3.05
pyrolyzed (30 min, 600 $^\circ C)$	raw OMW	0.84	323.50	386.50
pyrolyzed (30 min, 600 $^\circ C)$	SCO <sub>2</sub>	0.85	341.20	401.88
pyrolyzed (30 min, 600 $^\circ C)$	SCO <sub>2</sub> +EtOH	0.86	421.57	492.49
KOH activated (30 min, 800 $^\circ C)$	raw OMW	0.85	1305.42	1535.79
KOH activated (30 min, 800 $^\circ C)$	SCO <sub>2</sub>	0.86	1739.89	2023.13
KOH activated (30 min, 800 $^\circ C)$	SCO <sub>2</sub> +EtOH	0.86	1987.64	2319.30
KOH activated (30 min, 600 $^\circ C)$	raw OMW	0.85	809.64	952.51
KOH activated (30 min, 600 $^\circ C)$	SCO <sub>2</sub>	0.85	986.94	1161.11
KOH activated (30 min, 600 $^\circ C)$	SCO <sub>2</sub> +EtOH	0.88	984.86	1119.15
$\rm CO_2$ activated (40 min, 800 $^{\circ}\rm C)$	raw OMW	0.80	657.92	821.99
$CO_2$ activated (40 min, 800 $^\circ C)$	SCO <sub>2</sub>	0.85	684.71	800.93
$\rm CO_2$ activated (40 min, 800 $^\circ \rm C)$	SCO <sub>2</sub> +EtOH	0.82	742.91	905.98
$\rm CO_2$ activated (40 min, 600 $^{\circ}\rm C)$	raw OMW	0.84	328.85	390.55
$\rm CO_2$ activated (40 min, 600 $^{\circ}\rm C)$	SCO <sub>2</sub>	0.87	339.27	388.62
$\rm CO_2$ activated (40 min, 600 $^{\circ}\rm C)$	SCO <sub>2</sub> +EtOH	0.88	341.90	387.20
$\rm CO_2$ activated (120 min, 800 $^{\circ}\rm C)$	raw OMW	0.87	783.49	900.56
$\rm CO_2$ activated (120 min, 800 $^\circ \rm C)$	SCO <sub>2</sub>	0.86	713.70	829.89
$\rm CO_2$ activated (120 min, 800 $^{\circ}\rm C)$	SCO <sub>2</sub> +EtOH	0.85	575.16	676.66

**Carbon Content.** The carbon content of the OMW biochars (for specific surface area determination) was measured using a Mettler Toledo TGA-DSC-1 thermogravimetric analyzer (TGA). The instrument recorded temperature to 0.01 K and mass to 0.1  $\mu$ g every 10 s. The samples were heated to 110 °C under N<sub>2</sub> with a hold time of 30 min to remove moisture. The samples were then heated in N<sub>2</sub> to 910 °C at a rate of 100 °C/min and held for 30 min to ensure a stable mass loss reading to determine the volatile matter content (carbon available for adsorption).

**Surface Area Measurements.** Surface area was determined using a Micromeritics ASAP 2020 sorption analyzer. Approximately 400 mg of each sample was degassed at 300 °C for 10 h under vacuum to remove any gases and vapors on the surfaces of the sample. The untreated samples were degassed at 110 °C, as higher temperatures may cause devolatilization of organic matter that is removed in the pyrolysis step. The surface area was determined via nitrogen adsorption at 77 K via BET analysis using a minimum of 11 data points over a partial pressure range of 0.05–0.30; all samples had correlation coefficients ( $R^2$ ) for the BET isothermal of greater than 0.994, suggesting a 95% confidence in the data.<sup>36</sup>

**Functional Groups Using Fourier Transform Infrared Spectroscopy.** Analysis to determine the qualitative changes in surface functional groups upon activation of the OMW was carried out via Fourier transform infrared spectroscopy (FTIR) using a Nicolet Nexus 670 FT-IR with attenuated total reflectance (ATR). An aliquot of ground sample was placed on a zinc selenide crystal, and the ATR spectrum was taken, focusing on the wavenumber range from 4000 to  $500 \text{ cm}^{-1.37}$  The raw data were baseline corrected using a rubber-band baseline correction method. The data were then smoothed through 10 iterations of a Savitzky–Golay algorithm using 25 points. The resulting spectra were baseline corrected once more.

**Surface Characterization Using Scanning Electron Microscopy.** Qualitative analysis of the morphological surfaces of the raw, pyrolyzed, and activated samples was performed using scanning electron microscopy (SEM.) Samples were mounted on cylindrical copper mounts using a piece of carbon conductive tape and gold coated for 30 s using a Ladd 30800 sputter coater operating at 0.04 Torr and 20 mA. The coated samples were imaged using a JEOL JSV-5510-LV scanning electron microscope in high-vacuum mode with an accelerating voltage of 5 kV, a working distance of 22 mm, and a spot size of 30.

Adsorption of Contaminants from Water. To determine the affinity of the OMW ACs for heavy metals in water, we fabricated additional samples of raw and SCO2+EtOH OMW activated with both KOH (30 min, 600 °C) and CO<sub>2</sub> (40 min 800 °C). Given material and equipment constraints, we chose to use the raw and SCO<sub>2</sub>+EtOH, as the most likely biorefinery concept involving SCO<sub>2</sub> extraction would use ethanol as a co-solvent, given the considerably higher yield of polyphenols and ease of their recovery from ethanol.<sup>12</sup> Batch sorption experiments were performed in 15 mL glass vials using solutions of initial concentrations of Cd<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup> ranging from 1.5 to 15 mg/mL at room temperature (23.5 °C). These sorption experiments used 10.0 mL of solution with approximately 0.02 g of sorbent. We note that these concentrations are unrealistically high for environmental contamination scenarios, but they do allow for the collection of reproducible data, and comparison across the literature to similar studies. The pH values of all solutions were measured on a Mettler Toledo SevenExcellence meter and were within 4.9  $\pm$  0.1, at a suitable level to avoid metal ion precipitation. In addition, isotherms were measured using methylene blue (MB) dye (Acros Organics) over a concentration range of 0.04-1.6 mg/m using 10 mL of MB solution with between 0.005 and 0.006 g of sorbent. All sorption experiments were carried out at room temperature in a climate-controlled environment; temperatures were between 20.6 to 23.5 °C for the duration of the experiments.

Data were analyzed using Langmuir (eq 1), Freundlich (eq 2), and Temkin (eq 3) isotherms on STATA v.14; the "best fit" was assessed using correlation coefficient ( $R^2$ ) values to relate  $C_e$  and  $q_e$ , the equilibrium concentrations of adsorbate in solution and on adsorbent surface, respectively.

$$[q_e]_{\text{Langmuir}} = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{1}$$

 $q_{\rm m}$  and  $K_{\rm L}$  are the maximum adsorption capacity and equilibrium constant of adsorption associated with complete monolayer coverage.

$$[q_e]_{\text{Freundlich}} = K_F C_e^{1/n} \tag{2}$$

The constant  $K_{\rm F}$  indicates adsorption capacity, with 1/n representing the heterogeneity factor; n > 1 indicates favorable adsorption conditions for heterogeneous surfaces and multilayer adsorption.

$$[q_{\rm e}]_{\rm Temkin} = \frac{RT}{b} \ln(K_{\rm T}C_{\rm e}) = B \ln(K_{\rm T}C_{\rm e})$$
(3)

In this model, Temkin assumes that the heat of adsorption of molecules in a layer decreases linearly due to adsorbate—adsorbent molecules, with  $K_{\rm T}$  related to the maximum binding energy and *b* the heat of sorption, as a function of *R*, the universal gas constant, and *T*, the absolute temperature.<sup>38</sup>

Kinetic tests were carried out using initial stock concentrations of ~15 mg/L. Data were fit to pseudo-first-order (eq 4), pseudo-second-order (eq 5), and intraparticle diffusion (eq 6) models to assess the mechanism(s) controlling the overall rate of adsorption and determine rate constants (k) as a function of  $q_e$  and adsorption at time t,  $q_t$ .

$$\left\lceil \frac{\mathrm{d}q}{\mathrm{d}t} \right\rceil_{\mathrm{pseudo-first}} = k_1(q_e - q_t) \tag{4}$$

$$\left\lceil \frac{\mathrm{d}q}{\mathrm{d}t} \right\rceil_{\mathrm{pseudo-second}} = k_2 (q_{\mathrm{e}} - q_{\mathrm{t}})^2 \tag{5}$$

$$\left[q_{t}\right]_{\text{intraparticle}} = k_{i}t^{1/2} + D \tag{6}$$

D is proportional to the diffusional boundary layer thickness, and is thought to relate to the contribution of external mass transfer in controlling the rate of transport. Due to sorbent sample size limitations, kinetic experiments were only feasible with the metals, and not the dye.

Concentrations of each metal were determined using inductively coupled plasma mass spectrometry (ICP-MS) on an Agilent 7800 instrument using He at 5.0 mL/min. All samples were analyzed in immediate succession, with the instrument optimized using a fourelement tuning solution of Co, In, Li, and Tl in 2% HNO<sub>3</sub> from High Purity Standards. A calibration standard of 10  $\mu$ g/mL, including analytes of interest Cd<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup> in 2% HNO<sub>3</sub>, was purchased from the same supplier. Samples were diluted in a 2% HNO<sub>3</sub> matrix 2 h prior to analysis to be within the calibration range of 10–0.01  $\mu$ g/mL. Dye concentrations were measured on a Shimadzu UV-Vis 1800 instrument at 663 nm. Initial pH of all solutions ranged from 6.9 to 7.2.

# RESULTS AND DISCUSSION

Development of High Surface Area Materials. Biochars-pyrolyzed biomass samples-are known to possess relatively high surface areas, even without subsequent activation. In this instance, we see an increase of more than 2 orders of magnitude in BET surface area for pyrolyzed waste compared to untreated OMW. The supercritical extraction had a significant impact on pore development; the pyrolyzed raw OMW had a surface area of 323  $m^2/g_{sample}$ , compared to 341  $m^2/g_{sample}$  for SCO<sub>2</sub> pyrolyzed waste and 422  $m^2/g_{sample}$  for the SCO<sub>2</sub>+ÉtOH, as shown in Table 1. With the exception of the 120 min, 800 °C CO2 activated samples, the samples extracted with SCO<sub>2</sub> and SCO<sub>2</sub>+EtOH had higher surface areas than the other samples across all activation treatments, though the size of the increase was not consistent. For example, the 800 °C KOH activated sample's surface area was 14% higher for the SCO<sub>2</sub> and 53% higher for the SCO<sub>2</sub>+EtOH sample over the raw OMW, whereas the SCO<sub>2</sub> and raw samples for the KOH 600 °C had approximately the same surface area, yet the SCO<sub>2</sub>+EtOH followed by KOH at 600 °C yielded a 22% increase in surface area over the other two samples. For CO<sub>2</sub> activation, we find at 600 °C very similar surface areas to the 600 °C pyrolyzed samples, and that heat-treating the CO<sub>2</sub> 800 °C samples beyond 40 min is unnecessary, and is in fact detrimental to the SCO<sub>2</sub>+EtOH OMW.

From SEM images (Figure 2) we see scant evidence of widespread morphological changes between the raw, pyrolyzed,







c. Raw OMW, KOH Activated at 800°C, 30min

d. SCO<sub>2</sub>+EtOH OMW, KOH Activated at 800°C, 30min (inset image scale bar =  $1 \mu m$ )

**Figure 2.** Selected SEM images of OMW samples across extraction pretreatments and activation methods; scale bar indicates 20  $\mu$ m. (Images of all samples are available in the Supporting Information.)

and CO<sub>2</sub> (800 °C, 120 min) samples if we compare each treatment to its initial sample (i.e., raw untreated vs raw pyrolyzed vs raw CO<sub>2</sub>.) However, it appears that  $SCO_2$ +EtOH treatment itself begins to develop a porous network, with fewer amorphous regions than the raw sample. As others observed, KOH activation produces a more highly porous network, showing smaller surface patterning and highly structured micropores.<sup>39</sup> Additional SEM images are available in the Supporting Information.

Examples throughout the literature show high BET surface areas for a variety of activated biochars, including OMW, and depend on the biomass precursor and specific activation conditions (temperature, activating agent, etc.). González et al. find surface areas of 813 m<sup>2</sup>/g for olive stone activated with steam at 850 °C.<sup>40</sup> Others found specific surface areas ranging from 1143 to 2870 m<sup>2</sup>/g<sub>carbon</sub> for OMW activated with water vapor at 800–950 °C, and from 880 to 2090 and from 679 to 1013 m<sup>2</sup>/g<sub>carbon</sub> for CO<sub>2</sub> and air activation, respectively, in the same temperature range.<sup>34</sup> OMW pyrolyzed at 800 °C and activated with a 4:1 KOH:sample ratio (twice KOH used here) and activated at 800 and 900 °C resulted in ACs with surface areas between 1334 and 2578 m<sup>2</sup>/g.<sup>41</sup> KOH-activated OMW with a surface area of 1462 m<sup>2</sup>/g adsorbed 263 mg<sub>MB</sub>/g, versus a sample with a surface area of 2578 m<sup>2</sup>/g absorbing 208 mg<sub>MB</sub>/g.<sup>41</sup>

The surface areas obtained here are of great interest for several applications, including our future work on bioelectrodes for microbial fuel cells, where a high surface area yields increased electron transfer to mediators or reducers, increasing efficiency and making AC a valid alternative to expensive catalysts like platinum.<sup>26</sup> Interestingly, though surface area is important in maximizing sites available for adsorption, it has previously been observed that surface area does not correlate directly to the adsorption capacity of ACs for model compounds such as MB.<sup>42</sup> Clearly, optimizing the byproduct conversion pathway requires more than simply increasing the

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Table

			Langmuir isotherm		Frei	undlich isotherm		pseudo-second-order kineti	ics
sample	model contaminant	$q_{\rm m}  ({\rm mg/g})$	$K_{\rm L}$ (L/mg)	$R^2$	$k_{\mathrm{F}}  [\mathrm{mg/g}  (\mathrm{L/mg})^{1/n}]$	и	$R^2$	$K_2$ (S <sup>-1</sup> )	$R^2$
HOX-WMO	Cd	$120.1 \pm 7.2$	$0.1401 \pm 0.0059$	0.9929	$12.82 \pm 0.05$	$1.233 \pm 0.081$	0.9803	$7.181 \times 10^{-2} \pm 3.506 \times 10^{-4}$	0.9998
	Co	$123.8 \pm 7.8$	$0.1335 \pm 0.0056$	0.9921	$12.73 \pm 0.05$	$1.222 \pm 0.079$	0.9819	$7.202 \times 10^{-2} \pm 3.382 \times 10^{-4}$	0.9998
	Cu	$113.8 \pm 3.2$	$0.1533 \pm 0.0034$	0.9984	$12.99 \pm 0.05$	$1.266 \pm 0.071$	0.9840	$7.222 \times 10^{-2} \pm 3.432 \times 10^{-4}$	0.9998
	Zn	$125.7 \pm 7.8$	$0.1406 \pm 0.0058$	0.9923	$13.49 \pm 0.05$	$1.222 \pm 0.078$	0.9821	$7.147 \times 10^{-2} \pm 3.407 \times 10^{-4}$	0.9998
	MB dye	$2757.0 \pm 22.3$	$7.5648 \pm 0.0287$	0.0349	$5.36 \pm 0.01$	1.163 0.071	0.9490		
EtOH-KOH	Cd	$121.4 \pm 8.6$	$0.1394 \pm 0.0070$	0.9899	$12.91 \pm 0.05$	$1.227 \pm 0.084$	0.9794	$6.870 \times 10^{-2} \pm 5.402 \times 10^{-4}$	0.9994
	Co	$124.2 \pm 9.7$	$0.1339 \pm 0.0070$	0.9879	$12.82 \pm 0.05$	$1\ 219\ \pm\ 0.082$	0.9804	$6.859 \times 10^{-2} \pm 5.285 \times 10^{-4}$	0.9995
	Cu	$115.7 \pm 6.0$	$0.1487 \pm 0.0059$	0.9947	$12.92 \pm 0.05$	$1.251 \pm 0.079$	0.9810	$6.869 \times 10^{-2} \pm 5.381 \times 10^{-4}$	0.9994
	Zn	$65.4 \pm 32.0$	$0.2735 \pm 0.1987$	0.5827	$12.05 \pm 0.09$	$1.418 \pm 0.129$	0.9081	$6.841 \times 10^{-2} \pm 5.100 \times 10^{-4}$	0.9995
	MB dye	$3199.1 \pm 40.0$	$11.2671 \pm 0.0056$	0.1794	$3.19 \pm 0.01$	$1.723 \pm 0.009$	0.8910		
OMW-CO <sub>2</sub>	Cd	$113.8 \pm 0.2$	$0.1541 \pm 0.0002$	1.0000	$13.04 \pm 0.05$	$1.269 \pm 0.069$	0.9848	$6.890 \times 10^{-2} \pm 1.313 \times 10^{-3}$	0.9967
	Co	$118.3 \pm 2.2$	$0.1429 \pm 0.0019$	0.9993	$12.82 \pm 0.05$	$1.250 \pm 0.069$	0.9854	$6.888 \times 10^{-2} \pm 1.386 \times 10^{-3}$	0.9964
	Cu	$92.7 \pm 15.7$	$0.2705 \pm 0.0645$	0.9461	$15.96 \pm 0.02$	$1.535 \pm 0.025$	0.9972	$6.860 \times 10^{-2} \pm 1.394 \times 10^{-3}$	0.9963
	Zn	$118.4 \pm 2.4$	$0.1545 \pm 0.0023$	0.9992	$13.64 \pm 0.04$	$1.259 \pm 0.066$	0.9864	$6.865 \times 10^{-2} \pm 1.260 \times 10^{-3}$	0.9970
	MB dye	$3478.0 \pm 12.2$	$18.8516 \pm 0.0044$	0.9677	$17.31 \pm 0.01$	$0.697 \pm 0.025$	0.8682		
EtOH-CO <sub>2</sub>	Cd	$117.6 \pm 2.7$	$0.1432 \pm 0.0025$	0.9989	$12.75 \pm 0.05$	$1.250 \pm 0.072$	0.9842	$6.749 \times 10^{-2} \pm 6.209 \times 10^{-4}$	0.9992
	Co	$120.8 \pm 2.5$	$0.1360 \pm 0.0020$	0.9991	$12.61 \pm 0.05$	$1.239 \pm 0.070$	0.9853	$6.747 \times 10^{-2} \pm 6.006 \times 10^{-4}$	0.9993
	Cu	$105.3 \pm 7.0$	$0.1820 \pm 0.0116$	0.9911	$13.65 \pm 0.04$	$1.333 \pm 0.054$	0.9899	$6.747 \times 10^{-2} \pm 5.966 \times 10^{-4}$	0.9993
	Zn	$122.4 \pm 1.6$	$0.1446 \pm 0.0013$	0.9997	$13.41 \pm 0.05$	$1.241 \pm 0.068$	0.9860	$6.732 \times 10^{-2} \pm 5.838 \times 10^{-4}$	0.9993
	MB dye	$3478.1 \pm 0.5$	$102.0252 \pm 0.0013$	0.7813	$21.26 \pm 0.01$	$1.353 \pm 0.026$	0.9945		
<sup>a</sup> Results for all 1	models are available in	the Supporting Infe	ormation.						

BET surface area. Another important component is the surface reactivity of the sorbent and its affinity for target adsorbates.

Surface Functional Groups. FTIR offers a semiquantitative comparison of major changes in surface functional groups as a result of the various treatment conditions applied to the raw and supercritical fluid extracted OMW. The FTIR spectra of the raw, SCO<sub>2</sub>, and SCO<sub>2</sub>+EtOH samples are shown in Figure S2 of the Supporting Information; supercritical fluid extraction had a significant impact on the surface functional groups of the samples. The absence of strong C=O bands between 1800 and 1650  $\text{cm}^{-1}$  for the raw, SCO<sub>2</sub>, and SCO<sub>2</sub>+EtOH samples suggests the presence of compounds with sp hybridization; given the strong signals between 2850 and 3000 cm<sup>-1</sup>, with weak signals at 1460 cm<sup>-1</sup>, this suggests sp<sup>3</sup> C—H stretching of aliphatic chains that are abundant in this material and other lignocellulosic biomasses. The presence of coupled peaks within this region, specifically at 2912 and 2879; 2923 and 2853; and 2923 and 2854 cm<sup>-1</sup> for the raw, SCO<sub>2</sub>, and SCO<sub>2</sub>+EtOH samples, respectively, suggest that these are C-H-O surface functional groups, and actually increase upon SCO<sub>2</sub> extraction. While we know that SCO<sub>2</sub> extraction removes aliphatic groups from the bulk material, it is conceivable that the extraction causes partial oxidation of carbon on the surface, explaining the presence of the C-H-O surface groups. Possible C=O groups present in the raw OMW decrease due to the SCO<sub>2</sub>, likely due to removal of the fatty acids and/or possible oxidation of the carbon surface during extraction.

The presence of one broad band between 3500 and 3300 cm<sup>-1</sup>, along with the small peaks between 1640 and 1550 cm<sup>-1</sup> indicates secondary amines and N-H bending, respectively.43 Given the weak signals for N-H bending, this indicates the presence of amines, rather than the stronger signal expected for amides. The presence of amine functional groups is slightly reduced by the SCO<sub>2</sub>+EtOH and significantly reduced by the SCO<sub>2</sub> treatment (and virtually absent from the pyrolyzed and activated samples). Supercritical treatments-both with and without ethanol as the co-solvent-reduce by orders of magnitude both the relative intensity and the width of peaks at 3383 cm<sup>-1</sup> for the raw sample and 3523 cm<sup>-1</sup> for the supercritical samples. This indicates the presence of -OH functional groups of polysaccharides.43 The broader peak and lower wavelength for the raw OMW are suggestive of stronger hydrogen bonding. Using these results as a "baseline" for each extraction treatment, we note changes in the relative intensities and peak shifts as a result of activation of the OMW samples; details of peak wavelengths assigned to various functional groups and relative peak intensity are given in Table S1 of the Supporting Information.

The aromatic -C-H nature of the untreated samples (at 852–840 cm<sup>-1</sup>) is relatively low (Table 2). However, the aromatic ring nature of the surface functional groups (870–810 cm<sup>-1</sup>) increased markedly upon pyrolysis, as well as for the partial oxidation using CO<sub>2</sub>. This is expected: aromatics are known to result from incomplete combustion and partial oxidation of carbonaceous materials<sup>44</sup> and have been demonstrated to form in biochars pyrolyzed at a variety of temperatures.<sup>42,45</sup>

The pyrolyzed samples (biochars) had significantly lower signals in the -OH stretching band; similar behavior is documented for a series of shell and stone biomasses.<sup>46</sup> However, all the activation treatments increased the relative intensity of -OH functional group peaks (between 3588 and

3327 cm<sup>-1</sup>) by an order of magnitude over untreated and pyrolyzed samples. Absorption bands between 3000 and 2850 cm<sup>-1</sup> likely correspond to sp<sup>3</sup>-hybridized C–H stretching<sup>47</sup> and show significant increases in absorption for all activation treatments, but most notably for the high-temperature KOH. Of note in this absorption region are double peaks between 3000 and 2850 cm<sup>-1</sup> seen only for the samples treated at 800 °C KOH and 600 °C CO<sub>2</sub>, suggesting –C–H stretching of saturated alkanes.

Activated samples show strong absorption between 1750 and 1650 cm<sup>-1</sup> and between 1500 and 1450 cm<sup>-1</sup>, representative of -C=O groups (ketones, aldehydes, carboxylic acids, amides, and esters). Given that the -C=O peaks are outside the narrow 1750 to 1735 cm<sup>-1</sup> band seen for most esters, coupled with modest peaks observed between 1350 and 1150 cm<sup>-1</sup>, it is unlikely that the raw or KOH 800 °C samples have a large amount of acyl or phenyl esters. The same rationale applies to the pyrolyzed samples between 1150 and 1000 cm<sup>-1</sup> and alkoxy esters.<sup>48</sup> Considering the -C=O groups and -C-H-O groups discussed above, it appears that the 800 °C KOH and 600 °C CO<sub>2</sub> treatments overall imparted more oxygencontaining surface functional groups than low-temperature KOH and high-temperature CO<sub>2</sub> treatments.

From Figure 3, we see that the relative number of oxygencontaining functional groups is not strongly influenced by the



Figure 3. Relative absorption of oxygen-containing surface functional groups by sample: (●) OH, 3600–3300 cm<sup>-1</sup>; (■) C=O, 1750–1650 cm<sup>-1</sup>; (×) C=O, 1500–1450 cm<sup>-1</sup>; (△) CO, 1350–1250 cm<sup>-1</sup>; and (+) CO, 1150–1000 cm<sup>-1</sup>.

 $SCO_2$ , but by the activation conditions. The high-temperature KOH and low-temperature  $CO_2$  techniques appear to encourage the formation of -C=O surface groups. The high-temperature KOH activation increased the relative amount of -OH groups present, though not to the degree observed for the 600 °C, 40 min and 800 °C, 120 min  $CO_2$  samples.

Applicability of OMW Sorbents to Wastewater Treatment. Equilibrium adsorption studies on the ability of four OMW-ACs to remove  $Cd^{2+}$ ,  $Co^{2+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$  and MB from water show maximum adsorption capacities ranging from 65 to 126 mg of each metal per gram of AC, with total adsorption capacities ranging from 425 to 483 mg<sub>metal</sub>/ gram<sub>OMW-AC</sub>, and from 2757 to 3478 mg of dye per gram of AC, as shown in Table 2. Samples most closely adhered to the Langmuir isotherm for the metal adsorption (with the exception of Zn for EtOH-KOH samples) as determined through correlation coefficients for each model. (Full adsorption study results are available in Table S1 and Figures S3 and S4 of the Supporting Information.) This suggests that



Figure 4. Equilibrium and kinetics adsorption of metals onto OMW-activated carbons (error bars indicate  $\pm$  one standard deviation).

adsorption of heavy metals is monolayer in nature, and as Freundlich isotherm adsorption intensity, n, values are all greater than 1, this suggests favorable adsorption for all samples, as is commonly seen for solid—liquid adsorption of metals on biomass-based ACs.<sup>38</sup> However, with the exception of the OMW-CO<sub>2</sub>, the dye adsorption was considerably better explained by the Freundlich isotherm, suggesting heterogeneous adsorption mechanisms that do not necessarily rely on monolayer interactions with surface functional groups as seen with the metal adsorption.

Prior research demonstrates that -OH,  $-COO^-$ , -CO, and  $-NH_2$  functional groups promote the adsorption of pollutants such as heavy metals and dyes on biochars and activated biomass-based sorbents.<sup>48–50</sup> The KOH-activated samples, with moderately higher -OH and lower C=O groups than the  $CO_2$ -activated samples used in adsorption studies, show moderately higher adsorption capacities (only statistically significant for OMW-KOH- versus  $CO_2$ -activated samples) for Cd and Cu, as seen in Figure 4. However, these samples also exhibited the highest surface areas, so it is not possible to attribute the increased adsorption capacity to physical or chemical mechanisms through these data alone.

The OMW-KOH-activated sample has a faster rate of adsorption for all four metals studied as compared to the other three samples, which are statistically indistinguishable (though trends suggest that EtOH-CO<sub>2</sub> may be sluggish in comparison to other samples.) The adsorption of all metals appears to follow pseudo-second-order kinetics as indicated by  $R^2 > 0.99$ for all samples,  $R^2 > 0.45$  for pseudo-first-order, and  $R^2 > 0.65$ for intra-particle diffusion models, as shown in Table S3 and Figure S5 of the Supporting Information. For all samples, adsorption of 75% of equilibrium capacity was reached within 5 min, suggesting that these samples would be practical and economically viable for large-scale adsorption applications. To check the accuracy of this statement, we ran kinetic experiments on remaining the OMW-CO<sub>2</sub> sample at times under 5 min. As shown in Figure S6, the adsorption of every metal is linear as a function of time under 5 min and is well represented by the adsorption predicted by pseudo-secondorder kinetics. We remind that reader that of course these heavy-metal concentrations are unrealistically high to represent environmental contamination scenarios. However, they shed

light on the impact—or lack thereof—of biochar precursor on resulting AC properties, and open lines of future research to explore the design of remediation strategies for heavy-metal and mixed contaminant systems using biomass-based ACs.

# CONCLUSIONS

Because of the drawbacks to traditional lagooning and use of OMW as fertilizer, we must identify economically and environmentally viable alternatives for managing the millions of tons of OMW generated annually in the Mediterranean basin. Through prior work we demonstrated that it is possible to recover lucrative concentrations of polyphenols and polyunsaturated fatty acids via CO2-supercritical fluid extraction, which was enhanced by using ethanol as a co-solvent. We further demonstrated that the activation energy barrier to produce biofuels from this altered waste was lowered by preextraction. This work shows that the solid waste remaining after pyrolysis of the supercritical fluid extracted material can be converted to a high surface area biomass-based activated carbon through two different activation schemes. Supercritical fluid extraction promotes an increase in surface area among raw, pyrolyzed, and KOH-activated samples, though it does not have a significant effect on CO<sub>2</sub>-activated samples. In addition, supercritical fluid extraction does not greatly impact the resulting surface functional groups after chemical and physical activation.

Extraction via supercritical  $CO_2$  (with and without ethanol as a co-solvent) does not hinder the transformation of the solid waste to adsorbents. In the case of KOH-activated samples, prior extraction only helps to increase the specific surface area. While it is not recommended to subject all potential biomasses to supercritical extraction prior to conversion to an AC, in this case the extracted biomass is a byproduct resulting from an upstream conversion, and was therefore investigated to determine if further products could result from this waste transformation. A subset of KOH- and CO2-activated samples demonstrated adsorption capacities upward of 400 mg of metal (Cd<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup>) per gram of AC. Adsorption studies indicate adsorption is monolayer in nature (following a Langmuir isotherm) according to pseudo-second-order kinetics, reaching 75% of equilibrium capacity in 5 min of contact. This renders the proposed integrated biorefinery for OMW

management feasible, including supercritical fluid extraction for recovery of organic compounds, pyrolysis and recovery of fuels, and fabrication of ACs for wastewater, as an alternative to traditional waste disposal. Future work on the economic feasibility of a scaled-up design for this integrated bio-refinery is ongoing, as well as the application of these biomass-based ACs to microbial and other fuel cell electrodes.

# ASSOCIATED CONTENT

## **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b02202.

Complete FTIR spectral information, adsorption isotherm kinetics analysis for individual samples, and additional SEM images of fabricated activated carbons (PDF)

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#### Notes

The authors declare no competing financial interest.

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# REFERENCES

(1) Faostat (Food and Agriculture Organization of the United Nations, Statistics Division), http://faostat3.fao.org/faostat-gateway/go/to/home/E (accessed July 2015).

(2) Di Giovacchino, L.; Sestili, S.; Di Vincenzo, D. Influence of olive processing on virgin olive oil quality. *Eur. J. Lipid Sci. Technol.* 2002, 104, 587–601.

(3) Saez, L.; Perez, J.; Martinez, J. Low molecular weight phenolics attenuation during simulated treatment of wastewaters from olive oil mills in evaporation ponds. *Water Res.* **1992**, *26* (9), 1261–1266.

(4) Vlyssides, A. G.; Loizides, M.; Karlis, P. K. Integrated strategic approach for reusing olive oil extraction by-products. *J. Cleaner Prod.* **2004**, *12* (6), 603–611.

(5) Martín-Peláez, S.; Covas, M. I.; Fitó, M.; Kušar, A.; Pravst, I. Health effects of olive oil polyphenols: recent advances and possibilities for the use of health claims. *Mol. Nutr. Food Res.* **2013**, 57 (5), 760–771.

(6) Obied, H. K.; Allen, M. S.; Bedgood, D. R.; Prenzler, P. D.; Robards, K.; Stockmann, R. Bioactivity and analysis of biophenols recovered from olive mill waste. *J. Agric. Food Chem.* **2005**, *53* (4), 823–837.

(7) Visioli, F.; Romani, A.; Mulinacci, N.; Zarini, S.; Conte, D.; Vincieri, F. F.; Galli, C. Antioxidant and other biological activities of olive mill waste waters. *J. Agric. Food Chem.* **1999**, *47* (8), 3397–3401.

(8) Capasso, R.; Cristinzio, G.; Evidente, A.; Scognamiglio, F. Isolation, spectroscopy and selective phytotoxic effects of polyphenols from vegetable waste waters. *Phytochemistry* **1992**, *31* (12), 4125–4128.

(9) Lesage-Meessen, L.; Navarro, D.; Maunier, S.; Sigoillot, J. C.; Lorquin, J.; Delattre, M.; Labat, M. Simple phenolic content in olive oil residues as a function of extraction systems. *Food Chem.* **2001**, 75 (4), 501–507.

(10) ElMekawy, A.; Diels, L.; Bertin, L.; De Wever, H.; Pant, D. Potential biovalorization techniques for olive mill biorefinery wastewater. *Biofuels, Bioprod. Biorefin.* **2014**, 8 (2), 283–293.

(11) Kurniawan, A.; Effendi, C.; Ong, L. K.; Ju, Y. H.; Lin, C. X.; Ismadji, S. Novel, Integrated Biorefinery Approach of Ceiba pentandra (Kapok) Seed and Its Secondary Waste. *ACS Sustainable Chem. Eng.* **2013**, *1* (5), 473–480.

(12) Schievano, A.; Adani, F.; Buessing, L.; Botto, A.; Casoliba, E. N.; Rossoni, M.; Goldfarb, J. L. An integrated biorefinery concept for olive mill waste management: supercritical CO2 extraction and energy recovery. *Green Chem.* **2015**, *17* (5), 2874–2887.

(13) Pütün, A. E.; Uzun, B. B.; Apaydin, E.; Pütün, E. Bio-oil from olive oil industry wastes: Pyrolysis of olive residue under different conditions. *Fuel Process. Technol.* **2005**, *87* (1), 25–32.

(14) Martin-Lara, M. A.; Pagnanelli, F.; Mainelli, S.; Calero, M.; Toro, L. Chemical treatment of olive pomace: Effect on acid-basic properties and metal biosorption capacity. *J. Hazard. Mater.* **2008**, *156* (1), 448–457.

(15) Veglio, F.; Beolchini, F.; Prisciandaro, M. Sorption of copper by olive mill residues. *Water Res.* **2003**, *37* (20), 4895–4903.

(16) Banat, F.; Al-Asheh, S.; Al-Makhadmeh, L. Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters. *Process Biochem.* **2003**, *39* (2), 193–202.

(17) Batzias, F. A.; Sidiras, D. K. Simulation of methylene blue adsorption by salts-treated beech sawdust in batch and fixed-bed systems. *J. Hazard. Mater.* **2007**, *149* (1), 8–17.

(18) Rafatullah, M.; Sulaiman, O.; Hashim, R.; Ahmad, A. Adsorption of methylene blue on low-cost adsorbents: a review. *J. Hazard. Mater.* **2010**, *177* (1), 70–80.

(19) Annadurai, G.; Ling, L. Y.; Lee, J. F. Adsorption of reactive dye from an aqueous solution by chitosan: isotherm, kinetic and thermodynamic analysis. *J. Hazard. Mater.* **2008**, *152* (1), 337–346.

(20) Sun, D.; Zhang, X.; Wu, Y.; Liu, X. Adsorption of anionic dyes from aqueous solution on fly ash. *J. Hazard. Mater.* **2010**, *181* (1), 335–342.

(21) Cabrita, I.; Ruiz, B.; Mestre, A. S.; Fonseca, I. M.; Carvalho, A. P.; Ania, C. O. Removal of an analgesic using activated carbons prepared from urban and industrial residues. *Chem. Eng. J.* **2010**, *163* (3), 249–255.

(22) Luo, X.; Lei, X.; Cai, N.; Xie, X.; Xue, Y.; Yu, F.; et al. Removal of heavy metal ions from water by magnetic cellulose-based beads with embedded chemically modified magnetite nanoparticles and activated carbon. *ACS Sustainable Chem. Eng.* **2016**, *4*, 3960–3969.

(23) Rivera-Utrilla, J.; Prados-Joya, G.; Sánchez-Polo, M.; Ferro-García, M. A.; Bautista-Toledo, I. Removal of nitroimidazole antibiotics from aqueous solution by adsorption/bioadsorption on activated carbon. *J. Hazard. Mater.* **2009**, *170* (1), 298–305.

(24) Yao, Y.; Gao, B.; Chen, H.; Jiang, L.; Inyang, M.; Zimmerman, A. R.; Li, H. Adsorption of sulfamethoxazole on biochar and its impact on reclaimed water irrigation. *J. Hazard. Mater.* **2012**, *209-210*, 408–413.

(25) Zheng, W.; Guo, M.; Chow, T.; Bennett, D. N.; Rajagopalan, N. Sorption properties of greenwaste biochar for two triazine pesticides. *J. Hazard. Mater.* **2010**, *181* (1), 121–126.

(26) Zhang, F.; Cheng, S.; Pant, D.; Bogaert, G. V.; Logan, B. E. Power generation using an activated carbon and metal mesh cathode in a microbial fuel cell. *Electrochem. Commun.* **2009**, *11* (11), 2177–2179.

(27) Antal, M. J.; Varhegyi, G.; Jakab, E. Cellulose pyrolysis kinetics: revisited. *Ind. Eng. Chem. Res.* **1998**, 37 (4), 1267–1275.

(28) Chattopadhyay, J.; Kim, C.; Kim, R.; Pak, D. Thermogravimetric characteristics and kinetic study of biomass co-pyrolysis with plastics. *Korean J. Chem. Eng.* **2008**, *25* (5), 1047–1053.

(29) Dunn, P. J. The importance of green chemistry in process research and development. *Chem. Soc. Rev.* 2012, 41 (4), 1452-1461.

(30) Di Blasi, C. Modeling chemical and physical processes of wood and biomass pyrolysis. *Prog. Energy Combust. Sci.* **2008**, 34 (1), 47–90.

(31) Encinar, J. M.; Gonzalez, J. F.; Martínez, G.; Roman, S. Catalytic pyrolysis of exhausted olive oil waste. *J. Anal. Appl. Pyrolysis* **2009**, 85 (1), 197–203.

(32) Dionisi, D.; Carucci, G.; Papini, M. P.; Riccardi, C.; Majone, M.; Carrasco, F. Olive oil mill effluents as a feedstock for production of biodegradable polymers. *Water Res.* **2005**, 39 (10), 2076–2084.

(33) Mameri, N.; Aioueche, F.; Belhocine, D.; Grib, H.; Lounici, H.; Piron, D. L.; Yahiat, Y. Preparation of activated carbon from olive mill solid residue. *J. Chem. Technol. Biotechnol.* **2000**, 75 (7), 625–631.

(34) Pin, J. M.; Guigo, N.; Mija, A.; Vincent, L.; Sbirrazzuoli, N.; van der Waal, J. C.; De Jong, E. Valorization of Biorefinery Side-Stream Products: Combination of Humins with Polyfurfuryl Alcohol for Composite Elaboration. ACS Sustainable Chem. Eng. 2014, 2 (9), 2182–2190.

(35) Le Floch, F.; Tena, M. T.; Rios, A.; Valcarcel, M. Supercritical fluid extraction of phenol compounds from olive leaves. *Talanta* **1998**, *46* (5), 1123–1130.

(36) Brunauer, S.; Emmett, P. H.; Teller, E. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 1938, 60 (2), 309–319.

(37) Han, X.; Wang, W.; Ma, X. Adsorption characteristics of methylene blue onto low cost biomass material lotus leaf. *Chem. Eng. J.* **2011**, *171* (1), 1–8.

(38) Unur, E. Functional nanoporous carbons from hydrothermally treated biomass for environmental purification. *Microporous Mesoporous Mater.* **2013**, *168*, 92–101.

(39) Angin, D.; Altintig, E.; Köse, T. E. Influence of process parameters on the surface and chemical properties of activated carbon obtained from biochar by chemical activation. *Bioresour. Technol.* **2013**, *148*, 542–549.

(40) González, J. F.; Román, S.; Encinar, J. M.; Martínez, G. Pyrolysis of various biomass residues and char utilization for the production of activated carbons. *J. Anal. Appl. Pyrolysis* **2009**, *85* (1), 134–141.

(41) Stavropoulos, G. G.; Zabaniotou, A. A. Production and characterization of activated carbons from olive-seed waste residue. *Microporous Mesoporous Mater.* **2005**, 82 (1), 79–85.

(42) El-Sheikh, A. H.; Newman, A. P.; Al-Daffaee, H. K.; Phull, S.; Cresswell, N. Characterization of activated carbon prepared from a single cultivar of Jordanian Olive stones by chemical and physicochemical techniques. *J. Anal. Appl. Pyrolysis* **2004**, *71* (1), 151–164.

(43) Nuhoglu, Y.; Malkoc, E. Thermodynamic and kinetic studies for environmentaly friendly Ni (II) biosorption using waste pomace of olive oil factory. *Bioresour. Technol.* **2009**, *100* (8), 2375–2380.

(44) Goldfarb, J. L.; Suuberg, E. M. Vapor pressures and enthalpies of sublimation of ten polycyclic aromatic hydrocarbons determined via the Knudsen effusion method. *J. Chem. Eng. Data* **2008**, *53* (3), 670–676. Liu, Y.; He, Z.; Uchimiya, M. Mod. Appl. Sci. **2014**, *9*, 246–253.

(45) Özçimen, D.; Ersoy-Meriçboyu, A. Characterization of biochar and bio-oil samples obtained from carbonization of various biomass materials. *Renewable Energy* **2010**, *35* (6), 1319–1324.

(46) Akar, T.; Tosun, I.; Kaynak, Z.; Ozkara, E.; Yeni, O.; Sahin, E. N.; Akar, S. T. An attractive agro-industrial by-product in environmental cleanup: Dye biosorption potential of untreated olive pomace. *J. Hazard. Mater.* **2009**, *166* (2), 1217–1225.

(47) Hsu, C.-P. S. Infrared spectroscopy. In *Handbook of instrumental techniques for analytical chemistry*; Settle, F. A., Ed.; Prentice Hall: Upper Saddle River, NJ, 1997.

(48) Martin-Lara, M. A.; Pagnanelli, F.; Mainelli, S.; Calero, M.; Toro, L. Chemical treatment of olive pomace: Effect on acid-basic properties and metal biosorption capacity. *J. Hazard. Mater.* **2008**, *156* (1), 448–457.

(49) Minamisawa, M.; Minamisawa, H.; Yoshida, S.; Takai, N. Adsorption behavior of heavy metals on biomaterials. *J. Agric. Food Chem.* **2004**, *52* (18), 5606–5611.

(50) Pavan, F. A.; Lima, E. C.; Dias, S. L.; Mazzocato, A. C. Methylene blue biosorption from aqueous solutions by yellow passion fruit waste. *J. Hazard. Mater.* **2008**, *150* (3), *703–712*.