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

Jillian L. Goldfarb, Li Buessing, Erica Gunn, Melissa Lever, Alexander Billias, Esteve Casoliba, Andrea Schievano, and Fabrizio Adani

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 CO₂ and KOH. Specific surface areas of the OMW biochars were over 2300 m²/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 CO₂. 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 CO₂ 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. 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. Most olive mills use a three-phase centrifugation system resulting in a large quantity of wastewater, high in antimicrobial activity, and a solid waste stream, known as pomace (referred to here as OMW). While polyphenols naturally present in olive oil may impart a variety of health benefits, these same polyphenols make the disposal and treatment of OMW and wastewater difficult due to their phytotoxic and bacteriostatic nature. 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. When substantial quantities of OMW are spread across agricultural land, the presence of these biophenols may be harmful to crops and soil microflora. 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.\textsuperscript{14}\textsuperscript{15}

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 (ω3/ω6) present in OMW using supercritical CO\textsubscript{2} extraction with ethanol co-solvent, and transform the remaining solid biomass via thermochemical conversion to energy and high surface area biochars (Figure 1).\textsuperscript{12} We demonstrated that there is no energy penalty for the conversion of supercritical CO\textsubscript{2}-extracted OMW into bio-oil from pyrolysis; such bio-oil has similar characteristics to petroleum counterparts.\textsuperscript{13}\textsuperscript{14}\textsuperscript{15} More importantly, we found that pyrolyzed samples had specific surface areas greater than 400 m\textsuperscript{2}/g\textsubscript{carbon} 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\textsubscript{2})-extracted OMW to treat metal-contaminated waste.

Activated carbons can be used for a variety of applications, including removal of heavy metals from wastewater streams via ion exchange\textsuperscript{14}\textsuperscript{15} and dye removal from process water.\textsuperscript{16}\textsuperscript{19} However, as Luo et al. note, we must find new resources for efficient, environmentally friendly adsorbents for removing heavy-metal ions from water,\textsuperscript{22} as many of today’s ACs are fossil-fuel-based. Biomass-based ACs can remove pesticides, pharmaceuticals, and endocrine-disrupting compounds from water.\textsuperscript{21}\textsuperscript{25} Another potential application for such materials is in the construction of low-cost electrode surfaces in bioelectrochemical systems, where AC is a promising substitute for platinum-based catalysts for oxygen reduction and an electrochemically active coating for bio-electrodes.\textsuperscript{26}

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.\textsuperscript{27}\textsuperscript{29} 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\textsuperscript{2}/gram—via physical activation of carbonized OMW.\textsuperscript{32} To the best of our knowledge, there have been no studies on bio-based ACs from OMW pyrolysis following SCO\textsubscript{2} extraction of the polyphenols. Moreover, there is no literature available concerning the performance of SCO\textsubscript{2}-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.\textsuperscript{34}

\section*{EXPERIMENTAL SECTION}

\textbf{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.\textsuperscript{12} Briefly, raw samples (OMW) were extracted with either pure supercritical CO\textsubscript{2} (SCO\textsubscript{2}) or supercritical CO\textsubscript{2} with ethanol as a co-solvent (SCO\textsubscript{2}+EtOH). Both extractions proceeded at a total pressure of 250 bar and 70 °C, with a CO\textsubscript{2} flow rate of 80 kg/h. The raw OMW load was 7300 g for the SCO\textsubscript{2} run, and 7260 g for the SCO\textsubscript{2}+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.\textsuperscript{35}

\textbf{Preparation of OMW Biochars.} The OMW raw, SCO\textsubscript{2} and SCO\textsubscript{2}+EtOH samples were ground in a ball mill and mechanically sieved to yield particles less than 125 μm 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\textsubscript{2} 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\textsubscript{2}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\textsubscript{2}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.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure1.png}
\caption{Integrated biorefinery concept for extraction of polyphenols from OMW followed by energy and biochar recovery (dotted boxes indicate potential byproduct/energy recovery).}
\end{figure}
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 μg every 10 s. The samples were heated to 110 °C under N₂ with a hold time of 30 min to remove moisture. The samples were then heated in N₂ 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 (R²) for the BET isotherm of greater than 0.994, suggesting a 95% confidence in the data.36

**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 400 cm⁻¹.37 The raw data were baseline corrected using a rubber-band correction to remove any gases and vapors on the surfaces of the sample. The ATR technique is able to correct for minor changes in pellet thickness, but it does not correct for orientation in the sample.38

**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 μg every 10 s. The samples were heated to 110 °C under N₂ with a hold time of 30 min to remove moisture. The samples were then heated in N₂ 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).

**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 CO₂ (40 min, 800 °C). Given material and equipment constraints, we chose to use the raw and SCO₂+EtOH, as the most likely biorefiner concept involving SCO₂ extraction would use ethanol as a co-solvent, given the considerably higher yield of polyphenols and ease of their recovery from ethanol.12 Batch sorption experiments were performed in 15 mL glass vials using solutions of initial concentrations of Cd²⁺, Co²⁺, Cu²⁺, and Zn²⁺ ranging from 1.5 to 15 mg/mL at room temperature (23.5 °C). These sorption experiments used 1.0 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 ± 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/mL 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 (R²) values to relate Cₐ and qₑ, the equilibrium concentrations of adsorbate in solution and on adsorbent surface, respectively.

\[
q_{e,\text{Langmuir}} = \frac{q_m C_v}{1 + K_{C_v} C_v} \tag{1}
\]

\[
q_{e,\text{Freundlich}} = K_C C_v^{1/n} \tag{2}
\]

The constant Kₐ indicates adsorption capacity, with 1/n representing the heterogeneity factor; n > 1 indicates favorable adsorption conditions for heterogeneous surfaces and multilayer adsorption.

**Table 1. Carbon Contents and Surface Areas of Untreated, Pyrolyzed, and Activated OMW Samples with Particle Sizes Less than 125 μm**

<table>
<thead>
<tr>
<th>Activation Technique</th>
<th>Sample Size (μm)</th>
<th>Carbon Content (mass fraction)</th>
<th>BET Surface Area (m²/gsample)</th>
<th>Specific BET Surface Area (m²/gcarbon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated raw OMW</td>
<td>125</td>
<td>0.85</td>
<td>2.47</td>
<td>2.91</td>
</tr>
<tr>
<td>untreated SCO₂</td>
<td>125</td>
<td>0.87</td>
<td>2.48</td>
<td>2.85</td>
</tr>
<tr>
<td>untreated SCO₂+EtOH</td>
<td>125</td>
<td>0.86</td>
<td>2.62</td>
<td>3.05</td>
</tr>
<tr>
<td>Pyrolyzed (30 min, 600 °C) raw OMW</td>
<td>125</td>
<td>0.84</td>
<td>323.50</td>
<td>386.50</td>
</tr>
<tr>
<td>Pyrolyzed (30 min, 600 °C) SCO₂</td>
<td>125</td>
<td>0.85</td>
<td>341.20</td>
<td>401.88</td>
</tr>
<tr>
<td>Pyrolyzed (30 min, 600 °C) SCO₂+EtOH</td>
<td>125</td>
<td>0.86</td>
<td>421.57</td>
<td>492.49</td>
</tr>
<tr>
<td>KOH activated (30 min, 800 °C) raw OMW</td>
<td>125</td>
<td>0.85</td>
<td>1305.42</td>
<td>1535.79</td>
</tr>
<tr>
<td>KOH activated (30 min, 800 °C) SCO₂</td>
<td>125</td>
<td>0.86</td>
<td>1739.89</td>
<td>2023.13</td>
</tr>
<tr>
<td>KOH activated (30 min, 800 °C) SCO₂+EtOH</td>
<td>125</td>
<td>0.86</td>
<td>1987.64</td>
<td>2319.30</td>
</tr>
<tr>
<td>KOH activated (30 min, 600 °C) raw OMW</td>
<td>125</td>
<td>0.85</td>
<td>809.64</td>
<td>952.51</td>
</tr>
<tr>
<td>KOH activated (30 min, 600 °C) SCO₂</td>
<td>125</td>
<td>0.85</td>
<td>986.94</td>
<td>1161.11</td>
</tr>
<tr>
<td>KOH activated (30 min, 600 °C) SCO₂+EtOH</td>
<td>125</td>
<td>0.85</td>
<td>984.86</td>
<td>1119.15</td>
</tr>
<tr>
<td>CO₂ activated (40 min, 800 °C) raw OMW</td>
<td>125</td>
<td>0.80</td>
<td>657.92</td>
<td>821.99</td>
</tr>
<tr>
<td>CO₂ activated (40 min, 800 °C) SCO₂</td>
<td>125</td>
<td>0.85</td>
<td>684.71</td>
<td>800.93</td>
</tr>
<tr>
<td>CO₂ activated (40 min, 800 °C) SCO₂+EtOH</td>
<td>125</td>
<td>0.82</td>
<td>742.91</td>
<td>905.98</td>
</tr>
<tr>
<td>CO₂ activated (40 min, 600 °C) raw OMW</td>
<td>125</td>
<td>0.84</td>
<td>328.85</td>
<td>390.55</td>
</tr>
<tr>
<td>CO₂ activated (40 min, 600 °C) SCO₂</td>
<td>125</td>
<td>0.87</td>
<td>339.27</td>
<td>388.62</td>
</tr>
<tr>
<td>CO₂ activated (40 min, 600 °C) SCO₂+EtOH</td>
<td>125</td>
<td>0.88</td>
<td>341.90</td>
<td>387.20</td>
</tr>
<tr>
<td>CO₂ activated (120 min, 800 °C) raw OMW</td>
<td>125</td>
<td>0.87</td>
<td>783.49</td>
<td>900.56</td>
</tr>
<tr>
<td>CO₂ activated (120 min, 800 °C) SCO₂</td>
<td>125</td>
<td>0.87</td>
<td>713.70</td>
<td>829.89</td>
</tr>
<tr>
<td>CO₂ activated (120 min, 800 °C) SCO₂+EtOH</td>
<td>125</td>
<td>0.86</td>
<td>575.16</td>
<td>676.66</td>
</tr>
</tbody>
</table>
[\frac{dq}{dt}]_{\text{pseudo-first}} = k_1(q_0 - q_t)

(4)

[\frac{dq}{dt}]_{\text{pseudo-second}} = k_2(q_0 - q_t)^2

(5)

[\frac{dq}{dt}]_{\text{intraparticle}} = k_D^{1/2} + D

(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 four-element tuning solution of Co, In, Li, and Ti in 2% HNO₃ from High Purity Standards. A calibration standard of 10 mg/mL, including analytes of interest Cd²⁺, Co²⁺, Cu²⁺, and Zn²⁺ in 2% HNO₃, was purchased from the same supplier. Samples were diluted in a 2% KOH activation produces a more highly 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. Additional SEM images are available in the Supporting Information.

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 mechanisms controlling the overall rate of adsorption and determine rate constants (k) as a function of qₜ and adsorption at time t, qₜ.

From SEM images (Figure 2) we see scant evidence of widespread morphological changes between the raw, pyrolyzed, and CO₂ (800 °C, 120 min) samples if we compare each treatment to its initial sample (i.e., raw untreated vs raw pyrolyzed vs raw CO₂). However, it appears that SCO₂+EтOH 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. 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 m²/g for olive stone activated with steam at 850 °C. Others found specific surface areas ranging from 1143 to 2870 m²/g for OMW activated with water vapor at 800–950 °C, and from 880 to 2090 and from 679 to 1013 m²/g for CO₂ and air activation, respectively, in the same temperature range. 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 m²/g. KOH-activated OMW with a surface area of 1462 m²/g adsorbed 263 mgMB/g, versus a sample with a surface area of 2578 m²/g adsorbing 208 mgMB/g.

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. 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. Clearly, optimizing the byproduct conversion pathway requires more than simply increasing the

\[
[q]_{TS_{\text{min}}} = \frac{RT}{b} \ln(K_r C) = B \ln(K_r C)
\]

(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_r 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.

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Table 2. Equilibrium Adsorption Isotherm and Kinetics Models for Metal Adsorption onto OMW Activated Biochars with $R^2 > 0.98^\text{a}$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Model contaminant</th>
<th>$q_m$ (mg/g)</th>
<th>$K_L$ (L/mg)</th>
<th>$R^2$</th>
<th>$K_F$ [mg/g (L/mg)$^{1/n}$]</th>
<th>$n$</th>
<th>$R^2$</th>
<th>$k_2$ (S$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMW-KOH</td>
<td>Cd</td>
<td>120.1 ± 7.2</td>
<td>0.1401 ± 0.0059</td>
<td>0.9929</td>
<td>12.82 ± 0.05</td>
<td>1.233 ± 0.081</td>
<td>0.9803</td>
<td>7.181 × 10$^{-2}$ ± 3.506 × 10$^{-4}$</td>
<td>0.9998</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>123.8 ± 7.8</td>
<td>0.1335 ± 0.0056</td>
<td>0.9921</td>
<td>12.73 ± 0.05</td>
<td>1.222 ± 0.079</td>
<td>0.9819</td>
<td>7.202 × 10$^{-2}$ ± 3.382 × 10$^{-4}$</td>
<td>0.9998</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>113.8 ± 3.2</td>
<td>0.1533 ± 0.0034</td>
<td>0.9984</td>
<td>12.99 ± 0.05</td>
<td>1.266 ± 0.071</td>
<td>0.9840</td>
<td>7.222 × 10$^{-2}$ ± 3.432 × 10$^{-4}$</td>
<td>0.9998</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>125.7 ± 7.8</td>
<td>0.1406 ± 0.0058</td>
<td>0.9923</td>
<td>13.49 ± 0.05</td>
<td>1.222 ± 0.078</td>
<td>0.9821</td>
<td>7.147 × 10$^{-2}$ ± 3.407 × 10$^{-4}$</td>
<td>0.9998</td>
</tr>
<tr>
<td></td>
<td>MB dye</td>
<td>2757.0 ± 22.3</td>
<td>7.5648 ± 0.0287</td>
<td>0.0349</td>
<td>5.36 ± 0.01</td>
<td>1.163 ± 0.071</td>
<td>0.9800</td>
<td>7.147 × 10$^{-2}$ ± 3.407 × 10$^{-4}$</td>
<td>0.9998</td>
</tr>
<tr>
<td>EtOH-KOH</td>
<td>Cd</td>
<td>121.4 ± 8.6</td>
<td>0.1394 ± 0.0070</td>
<td>0.9899</td>
<td>12.91 ± 0.05</td>
<td>1.227 ± 0.084</td>
<td>0.9794</td>
<td>6.870 × 10$^{-2}$ ± 5.402 × 10$^{-4}$</td>
<td>0.9994</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>124.2 ± 9.7</td>
<td>0.1339 ± 0.0070</td>
<td>0.9879</td>
<td>12.82 ± 0.05</td>
<td>1.219 ± 0.082</td>
<td>0.9804</td>
<td>6.859 × 10$^{-2}$ ± 5.285 × 10$^{-4}$</td>
<td>0.9995</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>1157 ± 6.0</td>
<td>0.1487 ± 0.0059</td>
<td>0.9947</td>
<td>12.92 ± 0.05</td>
<td>1.251 ± 0.079</td>
<td>0.9810</td>
<td>6.869 × 10$^{-2}$ ± 5.381 × 10$^{-4}$</td>
<td>0.9994</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>654 ± 32.0</td>
<td>0.2735 ± 0.1987</td>
<td>0.5827</td>
<td>12.05 ± 0.09</td>
<td>1.418 ± 0.129</td>
<td>0.9081</td>
<td>6.841 × 10$^{-2}$ ± 5.100 × 10$^{-4}$</td>
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</tr>
<tr>
<td></td>
<td>MB dye</td>
<td>3199.1 ± 40.0</td>
<td>11.671 ± 0.0056</td>
<td>0.1794</td>
<td>3.19 ± 0.01</td>
<td>1.723 ± 0.099</td>
<td>0.8910</td>
<td>6.841 × 10$^{-2}$ ± 5.100 × 10$^{-4}$</td>
<td>0.9995</td>
</tr>
<tr>
<td>OMW-CO$_2$</td>
<td>Cd</td>
<td>1138 ± 0.2</td>
<td>0.1541 ± 0.0002</td>
<td>1.0000</td>
<td>13.04 ± 0.05</td>
<td>1.269 ± 0.069</td>
<td>0.9848</td>
<td>6.890 × 10$^{-2}$ ± 1.313 × 10$^{-3}$</td>
<td>0.9967</td>
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<tr>
<td></td>
<td>Co</td>
<td>1183 ± 2.2</td>
<td>0.1429 ± 0.0019</td>
<td>0.9993</td>
<td>12.82 ± 0.05</td>
<td>1.250 ± 0.069</td>
<td>0.9854</td>
<td>6.888 × 10$^{-2}$ ± 1.386 × 10$^{-3}$</td>
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<tr>
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<td>Cu</td>
<td>927 ± 15.7</td>
<td>0.2705 ± 0.0645</td>
<td>0.9461</td>
<td>15.96 ± 0.02</td>
<td>1.535 ± 0.025</td>
<td>0.9972</td>
<td>6.860 × 10$^{-2}$ ± 1.394 × 10$^{-3}$</td>
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<tr>
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<td>Zn</td>
<td>1184 ± 2.4</td>
<td>0.1545 ± 0.0023</td>
<td>0.9992</td>
<td>13.64 ± 0.04</td>
<td>1.259 ± 0.066</td>
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<td>6.865 × 10$^{-2}$ ± 1.260 × 10$^{-3}$</td>
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<tr>
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<td>MB dye</td>
<td>3478.0 ± 12.2</td>
<td>18.8516 ± 0.0004</td>
<td>0.9677</td>
<td>17.31 ± 0.01</td>
<td>0.697 ± 0.025</td>
<td>0.8682</td>
<td>6.865 × 10$^{-2}$ ± 1.260 × 10$^{-3}$</td>
<td>0.9970</td>
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<tr>
<td>EtOH--CO$_2$</td>
<td>Cd</td>
<td>1176 ± 2.7</td>
<td>0.1432 ± 0.0025</td>
<td>0.9989</td>
<td>12.75 ± 0.05</td>
<td>1.250 ± 0.072</td>
<td>0.9842</td>
<td>6.749 × 10$^{-2}$ ± 6.209 × 10$^{-4}$</td>
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<tr>
<td></td>
<td>Co</td>
<td>1208 ± 2.5</td>
<td>0.1360 ± 0.0020</td>
<td>0.9991</td>
<td>12.61 ± 0.05</td>
<td>1.239 ± 0.070</td>
<td>0.9853</td>
<td>6.747 × 10$^{-2}$ ± 6.006 × 10$^{-4}$</td>
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<tr>
<td></td>
<td>Cu</td>
<td>1053 ± 7.0</td>
<td>0.1820 ± 0.0116</td>
<td>0.9911</td>
<td>13.65 ± 0.04</td>
<td>1.331 ± 0.054</td>
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<td>6.747 × 10$^{-2}$ ± 5.966 × 10$^{-4}$</td>
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<td>Zn</td>
<td>1224 ± 1.6</td>
<td>0.1446 ± 0.0013</td>
<td>0.9997</td>
<td>13.41 ± 0.05</td>
<td>1.241 ± 0.068</td>
<td>0.9860</td>
<td>6.732 × 10$^{-2}$ ± 5.838 × 10$^{-4}$</td>
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</table>
|              | MB dye            | 3478.1 ± 0.5 | 102.0252 ± 0.0013 | 0.7813 | 21.26 ± 0.01               | 1.353 ± 0.026 | 0.9945

$^\text{a}$Results for all models are available in the Supporting Information.
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 semi-quantitative 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, SC(2)O, and SC(2)O+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 cm\(^{-1}\) for the raw, SC(2)O, and SC(2)O+EtOH samples suggests the presence of compounds with sp hybridization; given the strong signals between 2850 and 3000 cm\(^{-1}\), with weak signals at 1460 cm\(^{-1}\), this suggests sp\(^{3}\) C—H stretching of aliphatic chains that are abundant in this material and other lignocellulosic biomass. The presence of coupled peaks within this region, specifically at 2912 and 2879; 2923 and 2853; and 2923 and 2854 cm\(^{-1}\) for the raw, SC(2)O, and SC(2)O+EtOH samples, respectively, suggest that these are C—H—O surface functional groups, and actually increase upon SC(2)O extraction. While we know that SC(2)O 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 SC(2)O 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\(^{-1}\), along with the small peaks between 1640 and 1550 cm\(^{-1}\), 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 SC(2)O+EtOH and significantly reduced by the SC(2)O 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\(^{-1}\) for the raw sample and 3523 cm\(^{-1}\) for the supercritical samples. This indicates the presence of —OH functional groups of polysaccharides.45 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\(^{-1}\)) is relatively low (Table 2). However, the aromatic ring nature of the surface functional groups (870—810 cm\(^{-1}\)) increased markedly upon pyrolysis, as well as for the partial oxidation using CO2. This is expected: aromatics are known to result from incomplete combustion and partial oxidation of carbonate materials44 and have been demonstrated to form in biochars pyrolyzed at a variety of temperatures.42,43

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.46 However, all the activation treatments increased the relative intensity of —OH functional group peaks (between 3588 and 3327 cm\(^{-1}\)) by an order of magnitude over untreated and pyrolyzed samples. Absorption bands between 3000 and 2850 cm\(^{-1}\) likely correspond to sp\(^{3}\)-hybridized C—H stretching43 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\(^{-1}\) seen only for the samples treated at 800 °C KOH and 600 °C CO2, suggesting —C—H stretching of saturated alkanes.

Activated samples show strong absorption between 1750 and 1650 cm\(^{-1}\) and between 1500 and 1450 cm\(^{-1}\), 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\(^{-1}\) band seen for most esters, coupled with modest peaks observed between 1350 and 1150 cm\(^{-1}\), 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\(^{-1}\) and alkoxy esters.48 Considering the —C=O groups and —C—H—O groups discussed above, it appears that the 800 °C KOH and 600 °C CO2 treatments overall imparted more oxygen-containing surface functional groups than low-temperature KOH and high-temperature CO2 treatments.

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

**Figure 3.** Relative absorption of oxygen-containing surface functional groups by sample: (○) O, 3600—3300 cm\(^{-1}\); (■) C=O, 1750—1650 cm\(^{-1}\); (×) C=O, 1500—1450 cm\(^{-1}\); (△) CO, 1350—1250 cm\(^{-1}\), and (+) CO, 1150—1000 cm\(^{-1}\).
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. However, with the exception of the OMW-CO$_2$ 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 $-\text{OH}$, $-\text{COO}^-$, $-\text{CO}$, and $-\text{NH}_2$ functional groups promote the adsorption of pollutants such as heavy metals and dyes on biochars and activated biomass-based sorbents. The KOH-activated samples, with moderately higher $-\text{OH}$ and lower $\text{C}==\text{O}$ 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$_2$ 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$_2$ 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-second-order 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 CO$_2$-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 pre-extraction. 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$_2$-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 CO$_2$-activated samples demonstrated adsorption capacities upward of 400 mg of metal (Cd$^{2+}$, Co$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$) 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**

**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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