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5 **Evaluating landfill leachate treatment by organic municipal solid waste-derived biochar**

6 **Abstract**

7 Transforming the organic fraction of municipal solid waste (OFMSW) into biochar to reduce
8 fugitive landfill emissions and control organic micropollutants (OMP) during landfill leachate
9 treatment could provide a new circular economy organics diversion approach. However, research
10 on landfill leachate treatment under consistent, representative conditions with biochar derived
11 from the wide range of OFMSW components is needed. Further, the competitive nature of leachate
12 dissolved organic matter (DOM) for biochar adsorption sites has not been examined. To this end,
13 biochars were produced from seven diverse OFMSW types and batch tested using two
14 representative organic contaminants. To evaluate leachate DOM impact on OMP removal and
15 fouling mitigation with biochar enhancement methods, experiments were performed with three
16 background matrices (deionized water, synthetic leachate, real leachate) and two enhancement
17 methods (ash-pretreatment, double-heating). Since evaluating all possible OFMSW feedstock
18 combinations is infeasible, fundamental relationships between individual feedstocks and biochar
19 properties were evaluated. Overall, biochar performance varied substantially; the dose to achieve
20 a given target removal spanned an order of magnitude between the OFMSW feedstocks. Also, the
21 presence of leachate DOM more negatively impacted the performance of all biochars relative to
22 the benchmark adsorbent activated carbon. Finally, the enhancement methods altered biochar pore
23 structure by increasing micropore and slightly decreasing non-micropore surface areas, resulting
24 in improved adsorption capacity (by 23 to 93%). By providing the basis for a low-cost, enhanced
25 leachate treatment method, this study could incentivize a novel organics diversion approach that
26 reduces climate change impacts, harvests energy from waste, and reduces landfill air emissions.

27 **1 Introduction**

28 Fugitive landfill gas emissions, which are mainly produced from the degradation of organic
29 material,¹ have a significant contribution to climate change. For example, in the United States,
30 landfill emissions are the third largest source of anthropogenic methane emissions.² To minimize

33 the negative impacts of landfilling, the desire to divert organics from landfills is increasing (e.g.,
34 the United States has many existing and upcoming regulations³). As a result, several organics
35 diversion approaches are being pursued,⁴ and many try to take advantages of the opportunity to
36 recover resources from the organic waste.^{5,6} Despite those efforts, organics diversion strategies
37 still lack widespread implementation.⁷ Thus, there is a need for additional organic waste
38 management strategies that can valorize this waste stream.

39 A growing approach for managing organic waste, especially woody feedstocks, is the use of
40 pyrolysis,^{8,9} where organic material undergoes a thermo-chemical decomposition process under
41 heated conditions in the absence of oxygen, to produce energy and biochar.¹⁰⁻¹² While there are
42 many possible uses of biochar,¹³ employing biochar derived from the organic fraction of municipal
43 solid waste (OFMSW) as adsorbents for on-site leachate treatment is a novel circular economy
44 opportunity.¹⁴ Currently, organic micropollutants (OMPs) are commonly removed from landfill
45 leachate using activated carbon,^{15,16} which can be expensive and is typically produced from non-
46 renewable resources, such as bituminous coal. Since biochar has been found to remove OMPs from
47 a variety of background matrices,¹⁷ biochar could be used in place of activated carbon. However,
48 to test the feasibility of this approach, more research is needed due to the complexity of the
49 feedstock, OFMSW, and the background matrix.

50 Landfill leachate is a complex background matrix because it contains high levels of dissolved
51 organic matter (DOM) with diverse characteristics.¹⁸⁻²⁰ Background DOM can reduce biochar
52 sorption capacity for targeted OMPs^{21,22} through multiple fouling mechanisms (e.g., direct
53 competition, pore blockage).^{23,24} To help mitigate the expected fouling effects due to landfill
54 leachate composition, biochar enhancement methods could be used to generate biochars with
55 greater OMP sorption capacities or resistance to DOM fouling.^{17,25} For example, ash-pretreatment
56 was found to improve biochar sorption capacity in drinking water, wastewater, and stormwater.¹⁷
57 Also, a double-heating enhancement led to a threefold increase in the adsorption efficiency of a
58 wood waste-derived biochar's ability to adsorb sulfamethoxazole.²⁵ While these enhancement
59 methods are promising, and full-scale technologies exist that could execute the double-heating
60 enhancement,²⁶ it is unknown if OFMSW-derived biochar could be further valorized by such
61 enhancements or if they are effective at treating landfill leachate.

62 OFMSW is a complex feedstock that is comprised of four main components (food waste,
63 yard trimmings, wood, and paper), and each category consists of a wide range of wastes; for

example, food waste includes coffee grounds, a material low in ash (1.3% by mass) and cellulose (12.4% by mass) contents,²⁷ to materials like nutshells that are higher in ash (6.3%)²⁸ and cellulose (25-30%)²⁹ contents. Multiple waste streams (e.g., eucalyptus leaf residue,³⁰ waste-art-paper,³¹ MSW,^{32,33} paper sludge,³⁴ and wheat husk³⁴) have been used to produce biochar adsorbents, but many wastes found in OFMSW have not yet been used to make biochar adsorbents. This is likely because OFMSW has a heterogeneous composition that is constantly changing spatially and temporally. Since evaluating the performance of biochar produced from the unlimited potential combinations of OFMSW would be impractical, characteristics of individual feedstocks first need to be correlated with biochar characteristics to (i) help reduce the number of waste combinations that need to be evaluated experimentally based on a mechanistic understanding of biochar performance impacts, (ii) elucidate expected performance ranges for different mixtures, and (iii) produce the highest performing biochar adsorbents by selecting certain OFMSW components, especially those that are most feasible to collect separately (e.g., office paper, yard waste, wood construction waste).

Overall, how to best implement the proposed organics diversion strategy is unclear. While previous studies have examined OMP adsorption with waste-derived biochars,³³⁻³⁷ their differences between production conditions and experimental approaches, along with a lack of systematic understanding of OFMSW variability on biochar properties, shows the need to test the ability of OFMSW-derived biochar to treat landfill leachate. To this end, seven diverse OFMSW components were selected and used to produce biochars. Those biochars were directly compared to a commercial activated carbon in their ability to remove two representative contaminants, nitrobenzene and dichlorophenoxyacetic acid (2,4-D), from landfill leachate. To navigate the heterogeneous and variable nature of OFMSW and provide predictive insight on resulting biochar quality, associations between feedstock and biochar properties, including adsorption capacity, were evaluated. The biochars' adsorption capacities were evaluated in three background matrixes (deionized water, synthetic leachate, and real leachate) to understand the competitive nature of leachate DOM. The impacts of ash-pretreatment and double-heating were also examined. This research provides a basis for OFMSW beneficial use pathways because pyrolyzing OFMSW simultaneously produces biochar, harvests energy from waste, supports organics diversion efforts and regulations, and reduces fugitive landfill greenhouse gas emissions.

94 **2 Methods**

95 **2.1 Feedstock and Activated Carbon Selection**

96 The composition of typical OFMSW was investigated to determine the most representative
97 wastes to use as feedstocks for biochar production. About 60% of MSW is comprised of organic
98 material, which consists of about 25% paper and paperboard, 15% food waste, 13% yard
99 trimmings, and 7% wood.³⁸ Given the large number of biochar feedstock options within each
100 category and the variability in composition of municipal solid waste, one to three common and
101 abundant waste materials were chosen to represent each category.

102 Office paper was chosen to represent the paper and paperboard category. It was collected
103 from recycling bins and cut into 4-inch circles to match the pyrolysis crucible dimensions and
104 minimize air space during pyrolysis. For the more diverse food waste category, peanut shells,
105 orange peels, and spent coffee grounds were chosen. Peanuts were collected from a local
106 restaurant, shelled, and pulverized to minimize air space during pyrolysis. Orange peelings
107 collected from ripe oranges purchased from a local grocery store were cut into inch-wide pieces.
108 Spent coffee grounds were collected from a drip-coffee machine at a local coffee shop.

109 Grass and pine needles were chosen to represent the yard trimmings category. Pine wood
110 pellets were selected to represent the wood category. Soft-stem grass (90% Perennial Rye and 10%
111 Kentucky bluegrass) were cut and pulverized. Pine needles were collected from under an Austrian
112 Pine and pulverized. Dried pine wood pellets were purchased from Black Hill Gold (Spearfish
113 Pellet Company; Spear fish, SD) and pyrolyzed as received. Orange peels, spent coffee grounds,
114 grass, and pine needles were all dried at 105 °C for 24 hours prior to pyrolysis to reduce moisture
115 contents associated with these feedstocks. Activated carbon (Norit 1240) was chosen as a
116 benchmark adsorbent given its widespread use for sorption of OMPs.^{39,40}

117 **2.2 Biochar Production and Characterization**

118 Biochar was produced by pyrolyzing feedstocks and then grinding the resulting char,
119 following established methods.^{21,41,42} Each feedstock was packed into 450 mL covered crucibles
120 and pyrolyzed in a muffle furnace at 850 °C for 2 hours.^{21,41,43–45} This approach is representative
121 of many full-scale pyrolysis operations, which do not conduct nitrogen purging.⁴⁶ Resulting
122 biochars were ground with a mortar and pestle and wet-sieved to particle sizes between 38 and 75

123 μm (200 and 400 sieve size) and dried at 105 °C for at least 24 hours.¹⁷ This grinding and drying
124 was also used to produce powdered activated carbon (PAC).

125 Two proven biochar enhancement methods were used: ash-pretreatment and double-
126 heating.^{17,25,26} One feedstock from each OFMSW categories of paper, orange for food, grass for
127 yard trimmings, and wood, were enhanced. Ash-pretreatment involved soaking 200 g of each
128 feedstock in a solution of 2 g/L ash dissolved in deionized (DI) water for 12 hours and drying for
129 at least 24 hours at 105 °C before pyrolysis.¹⁷ The ash was produced by heating uncovered pine
130 wood pellets (Confluence Energy; Kremmling, CO) at 550°C for 6 hours. All ash-pretreated
131 biochars were pretreated with the same ash to reduce potential effects of ash composition
132 variability between feedstocks. The double-heating enhancement was conducted by re-heating
133 ground biochar in a 15 mL crucible covered with aluminum foil at 600 °C in the muffle furnace
134 for 2 hours.²⁵

135 Pyrolysis yield and feedstock density were measured by weighing the mass of each
136 feedstock before and after pyrolysis. Ash contents of the feedstocks and biochars were measured
137 by weighing the mass of each material before and after they were heated uncovered at 550 °C for
138 6 hours. The carbon (C), hydrogen (H), and nitrogen (N) content of each biochar was measured
139 using a CHN Elemental Analyzer (Perkin-Elmer model 2400).⁴⁷ The oxygen (O) content was
140 assumed to be the difference between the total mass and sum of the C, H, N, and ash contents.⁴⁸
141 Additionally, several ratios were calculated: H/C as an indicator for aromaticity as well as O/C
142 and (O+N)/C as a indicators for polarity. Average cellulose and lignin feedstock contents found in
143 the literature^{27–29,49–60} are reported in the Electronic Supplementary Information (ESI) Table S1.

144 2.3 Real and Synthetic Landfill Leachates

145 Biochar adsorption performance was tested in real landfill leachate, synthetic landfill
146 leachate, and DI water. The real leachate was collected from a local landfill in 1 L amber bottles,
147 passed through a 0.45 μm filter to remove particulate matter and then stored in air-tight amber
148 bottles at 4 °C. Since leachate can degrade over time,⁶¹ the ultraviolet absorption at 254 nm
149 (UVA₂₅₄) and the sorption performance of the most common biochar, wood biochar, was measured
150 daily; neither changed more than 10% between the first and third (last) day (e.g., UVA₂₅₄ changed
151 by 0.15%).

152 The synthetic leachate was modified from an established recipe^{18,19} by decreasing volatile
153 fatty acid (VFA) concentrations to a total chemical oxygen demand (COD) of 6000 mg/L and

154 substituting the original recipe's non-VFA organic compounds with the two representative OMPs,
155 nitrobenzene and 2,4-D. The synthetic leachate was representative of real leachate water quality
156 with respect to most constituents including ionic strength and chemical oxygen demand but
157 excluded the complex mixture of leachate-derived DOM matter (Table S2). The synthetic leachate
158 was also stored in air-tight amber bottles at 4°C for up to three days prior to batch testing. The pH,
159 UVA₂₅₄, and COD of the synthetic leachate did not change more than 10% over three days (e.g.,
160 pH varied by less than 4.5% and COD, measured using by less than 6.8%).

161 OMP adsorption performance tests were conducted with nitrobenzene and 2,4-D,
162 representing industrial and pesticide contaminants often found in landfill leachate. Nitrobenzene
163 is neutral and 2,4-D, which has a pKa of 2.73, is anionic in landfill leachate. Both are aromatic.
164 Additionally, both have small logK_{ow} values, so they are expected to be more difficult to remove
165 from water by carbonaceous adsorbents relative to the more hydrophobic OMPs often found in
166 landfill leachate.⁶²

167 Since OMPs are typically found in landfill leachate in the low parts per billion range,⁶³
168 radiolabeled nitrobenzene and 2,4-D were spiked into the background matrix at 30 µg/L each and
169 measured by liquid scintillation counting (LSC). Because DOM concentrations exceeded that of
170 the OMPs by several orders of magnitude, sorption performance was assessed on a percent OMP
171 removal basis and was independent of the OMP's initial concentration.⁶⁴ LSC samplers were
172 prepared by adding 4 mL of sample to an LSC vial with 10 mL of Ultima Gold™ scintillation
173 cocktail. For DI water, synthetic leachate, and real leachate, the detection limits for 2,4-D were
174 0.9, 0.8, and 2.4 µg/L, respectively, and for nitrobenzene were 5.3, 4.4, and 5.0 µg/L, respectively.

175 **2.4 Dose Response Curves**

176 Dose response curves were developed from 3-hour batch tests with spiked radiolabeled
177 OMPs;¹⁷ each adsorbent was dosed from a slurry to a 40 mL vial containing either real leachate,
178 synthetic leachate, or DI water that was spiked with radiolabeled 2,4-D and nitrobenzene. Vials
179 were mixed end-over-end in a tumbler at 13 rpm for 3 hours and filtered with 1.2 µm glass filters.
180 Six adsorbent doses between 16 and 512 mg/L were used in duplicate to target OMP removals
181 between 20% and 80%. 2,4-D removal required such large doses that the full dose-response curve
182 in real leachate was not fully characterized for all biochars.

183 **2.5 Data Analysis**

184 To identify potential correlations, a systematic approach of visually and statistically
185 evaluating all pairs and any combinations of parameters that had mechanistic basis was used. In
186 summary, those parameters were: two micropollutants (2,4-D, nitrobenzene), seven biochar
187 feedstocks (paper, pine needles, grass, wood, peanut shells, orange peels, coffee grounds), three
188 biochar production conditions (untreated, ash-pretreatment, double-heating), eight biochar
189 characteristics (%C, %H, %N, %O, %Ash, H/C, O/C, (O+N)/C), 11 feedstock characteristics
190 (%C, %H, %N, %O, %Ash, H/C, O/C, (O+N)/C, %lignin, %cellulose, %hemicellulose), three
191 background matrices (real landfill leachate, synthetic landfill leachate, DI water), and multiple
192 target removals (i.e., dose to 25% removal, dose to 50% removal).

193

194 **3 Results and Discussion**

195 **3.1 Evaluating Biochar Performance**

196 Biochar performance varied greatly (Table 1). The dose of adsorbent required to remove
197 50% of nitrobenzene and 25% of 2,4-D from real leachate was calculated by interpolating along
198 the dose response curves and allowed for direct comparison of adsorbent performance for each
199 OMP. For the biochars, the 50% removal of nitrobenzene in real leachate spanned an order of
200 magnitude from 25 to 728 mg/L. The 25% removal of 2,4-D resulted in an even larger dose range
201 of 120 to 6500 mg/L (Figure 1). Since so many unique waste feedstocks were compared side-by-
202 side and resulted in greatly varying biochar performance, the differences between the feedstocks
203 and resulting biochars were evaluated to elucidate properties that could help streamline feedstock
204 selection.

205 By design, the feedstocks selected were diverse in type and chemical composition. For
206 example, the feedstocks' measured ash contents varied from 2.0% (coffee) to 28% (peanut),
207 measured carbon contents from 44% (grass) to 57% (coffee), and estimated cellulose contents from
208 18% (coffee) to 81% (paper) (Table S1). The resulting biochars also had diverse traits. For
209 example, the biochars' composition of ash ranged from 1.2% (wood biochar) to 16% (grass
210 biochar), O:C ratios from 3.3 (paper biochar) to 15 (grass biochar), and H:C ratios from 9.2 (paper
211 biochar) to 21 (grass biochar) (Table 1). In particular, the biochars had a wide range of pore size
212 distributions and surface areas. For instance, the biochar's BET surface areas spanned from 23

213 m^2/g (coffee biochar) to 450 m^2/g (wood biochar) and micropore surface areas from 0 m^2/g (peanut
214 biochar) to 270 m^2/g (paper biochar) (Table 1).

215 Despite this diversity of characteristics and the extensive data analysis, which involved
216 evaluating over 100 different correlations, none of the feedstock characteristics had a strong
217 correlation with any of the biochar characteristics. There was only one weakly positive correlation
218 between biochar micropore surface area and the estimated feedstock cellulose content (Figure S1=,
219 $R^2 = 0.54$), even though a wide range of feedstock characteristics, including those known to
220 contribute to biochar structure were evaluated. For example, previous research with pure cellulose
221 and lignin mixtures have indicated that the volatilization of cellulose can facilitate pore
222 development, but that lignin must also be present to maximize surface area,^{65,66} but this OFMSW
223 biochar dataset did not find any correlations between those feedstock and biochar properties.
224 Similarly, there was a lack of strong correlations with biochar performance. Micropore surface
225 area, which was associated with cellulose, had a potential correlation with nitrobenzene removal
226 (Figure S2, $R^2 = 0.50$); previous research found that biochar made from cellulose can have a high
227 sorption affinity for nitrobenzene at low concentrations.^{65,66} There were no feedstock or biochar
228 properties that correlated with 2,4-D removal, likely due to the differences of OMP diffusivities,⁶⁷
229 sizes (nitrobenzene is smaller), and ionic state (2,4-D was anionic, nitrobenzene neutral).

230 Overall, the various feedstocks considered led to drastically different biochars, but
231 correlations between their properties were limited, consistent with previous efforts to identify such
232 linkages.^{21,47} Thus far, the lack of correlations hinders the ability to predict how biochars produced
233 from differing feedstocks would perform. However, since others have found that production
234 conditions can more strongly correlate with biochar performance,^{21,47} two enhancement methods
235 were explored next. These methods also had the potential benefit of improving biochar
236 performance, which was not competitive with activated carbon (Table 1) (e.g., PAC's dose for
237 50% nitrobenzene removal in real leachate was 7 mg/L while the best performing non-enhanced
238 biochar's dose was 42 mg/L; PAC's dose for 25% 2,4-D removal was 9 mg/L while the best
239 performing non-enhanced biochar's dose was 150 mg/L).

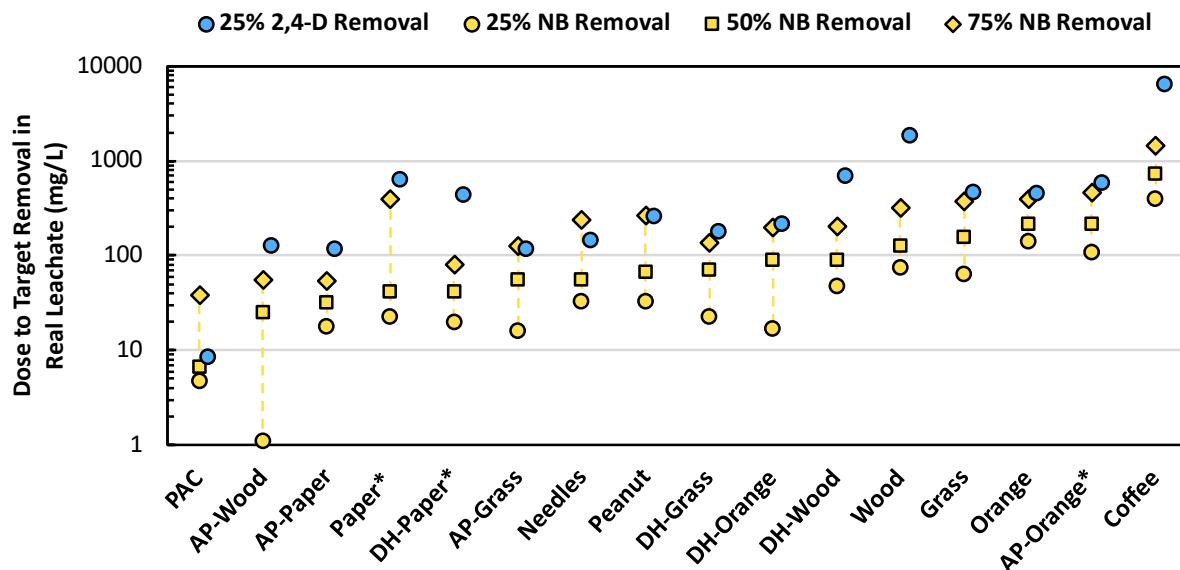
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242 **Table 1.** Performance in real leachate and physicochemical properties for each adsorbent,
243 including the ash-pretreated (AP) and double-heated (DH) biochars. Yellow horizontal bars
244 indicate dose to 50% removal of nitrobenzene (NB) in real leachate. All percentages are on a mass

245 basis. H/C represents hydrogen to carbon ratio. O/C represents oxygen to carbon ratio. Note: *
 246 denotes extrapolated values.

Adsorbent	Dose to 50% NB Removal in Real Leachate (mg/L)	Dose to 25% 2,4-D Removal in Real Leachate (mg/L)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Oxygen (%)	Ash (%)	H/C	O/C	Micropore Surface Area (m ² /g)	Non-micropore Surface Area (m ² /g)	BET Surface Area (m ² /g)
PAC	7	9	83	0.5	0.5	7.7	8.0	7.7	7.0	780	220	990
AP-Wood Biochar	25	130	89	0.6	0.2	8.6	1.7	8.6	7.2	420	150	570
AP-Paper Biochar	32	120	72	0.6	0.1	8.5	19	9.1	8.8	340	130	470
Paper Biochar	42	660	82	0.6	0.2	3.6	14	9.2	3.3	270	150	410
DH-Paper Biochar	42	450*	80	0.6	0.1	4.6	15	8.5	4.3	320	120	440
AP-Grass Biochar	55	120	53	1.2	3.3	14	28	26	19	130	110	240
Needles Biochar	56	150	78	0.9	1.5	11	8.7	14	10	170	140	310
Peanut Biochar	67	260	78	1.1	1.5	12	7.6	16	11	0	77	77
DH-Grass Biochar	70	180	70	1.3	4.4	2.3	22	21	2.5	43	32	75
DH-Orange Biochar	89	220	83	0.9	2.4	5.7	8.2	13	5.1	94	88	180
DH-Wood Biochar	91	700	85	0.7	0.2	13	1.3	9.3	11	320	140	460
Wood Biochar	127	1900	84	0.7	0.2	14	1.2	9.5	12	240	210	450
Grass Biochar	157	470	65	1.2	4.0	13	16	21	15	13	33	46
Orange Biochar	213	460	79	0.9	2.3	11	7	14	10	10	83	93
AP-Orange Biochar	216	600	77	1.0	2.1	12	7.6	15	12	56	63	120
Coffee Biochar	728	6500*	80	1.0	3.1	12	4.4	15	11	3.8	20	23

247
 248
 249



250
 251 **Figure 1.** Representation of the dose response curves for the removal of 2,4-D (blue)
 252 and nitrobenzene (NB) (yellow) in real leachate for each adsorbent, including the ash-pretreated (AP)
 253 and double-heated (DH) biochars. Dose response curve values include 25% (circles), 50%
 254 (squares), and 75% (diamonds) removals. Note: * denotes extrapolated values for 25% 2,4-D
 255 removal.

256

257 **3.2 Improving Biochar Performance**

258 In general, the double-heating and ash-pretreatment enhancement methods improved
259 sorption capacity (i.e., reduced biochar doses for the target removals of both OMPs) in real leachate
260 (Figure 2). Of the four feedstocks (wood, paper, grass, and orange) evaluated, the ash-pretreated
261 wood biochar had the greatest performance improvement; for example, the ash-pretreatment
262 enhancement reduced wood biochars 50% nitrobenzene removal dose by fivefold to 25 mg/L,
263 making it more similar to the PAC dose of 7 mg/L (Table 1). When comparing the impacts of each
264 enhancement method, the ash-pretreatment enhancement resulted in greater performance
265 improvements, but the impact was less consistent across the feedstocks (Figure 2); for example,
266 the ash-pretreatment enhancement led to worse performance with the ash-pretreated orange
267 biochar for 2,4-D. Despite performance inconsistencies within and between the enhancement
268 methods and feedstocks, enhancing biochar has the potential to significantly improve sorption
269 performance.

270 These performance improvements occur potentially because both enhancements altered the
271 biochars' pore structure (Figure 2). Specifically, the micropore surface area was increased for all
272 enhanced biochars, which has been observed before.^{25,68} Also, the non-micropore surface area
273 decreased with both enhancement methods for all but two enhanced biochars (ash-pretreated grass
274 and double-heated orange). This increase of micropore surface area, coupled with a slight
275 reduction in non-micropore surface area, has been observed before.²⁵ While biochar performance
276 did generally improve with the enhancements, the pore structure changes were not correlated with
277 changes in performance (Figure 2). This is likely due to the different impacts of different pore
278 changes; for example, increasing micropores can provide more primary OMP sorption sites;
279 decreasing non-micropores can lead to less DOM accommodation^{69–71} and more direct site
280 competition between DOM and OMPs for micropore sorption sites.^{23,70,72,73}

281 Since real leachate has a large variety and amount of DOM that can impact fouling, the
282 biochar enhancement impacts were next evaluated in a synthetic leachate with a controlled and
283 specified amount of DOM that consisted mostly of VFAs (Table S2) to represent the most
284 prevalent DOM fraction of real leachates.^{18,19} Biochar doses in synthetic leachate were so much
285 smaller than those in real leachate (Figure S3) that they were similar to those in water without any
286 DOM (i.e., DI water) (Figure S4). This suggests that the synthetic leachate had relatively minimal

287 DOM fouling and that the competitive effects from real leachate were dominated by non-VFA
288 DOM.

289 Biochars were more negatively impacted by real leachate's non-VFA DOM than PAC
290 (Figure 3). Despite the possibility that more non-micropore surface area can increase the ability to
291 mitigate DOM impacts,^{69–71} there was no trend between non-micropore surface area and the
292 increase in dose needed from the VFA-dominated DOM synthetic leachate to the real leachate with
293 much more diverse DOM components. Further, the amount of non-micropore surface area did not
294 correlate with adsorbent performance (Figure S5**Error! Reference source not found.**). Therefore,
295 changing non-micropore surface area via an enhancement may not impact biochar performance in
296 this context, especially due to the unique biochar response to the real leachate's non-VFA DOM.
297 Focusing on understanding that DOM, and its interactions with other OMPs, could help identify
298 enhancement approaches capable of making biochars more competitive with activated carbon in
299 landfill leachate.

300 On the other hand, increasing the micropore surface area may have been a main reason
301 why the enhancements improved sorption performance in both the real and synthetic leachates
302 (Figures 2 and 4, respectively). Since synthetic leachate had relatively minimal DOM fouling, the
303 biochar performances in that matrix can help isolate the impact of increasing micropore surface
304 area. In synthetic leachate, the sorption capacity for both OMPs was generally better (i.e., required
305 lower doses) with larger micropore surface areas (Figure 4). However, since the amount of
306 micropore surface increase due to either enhancement does not seem to predict the amount of
307 biochar performance change, this pore change was likely only part of the enhancements'
308 mechanisms.

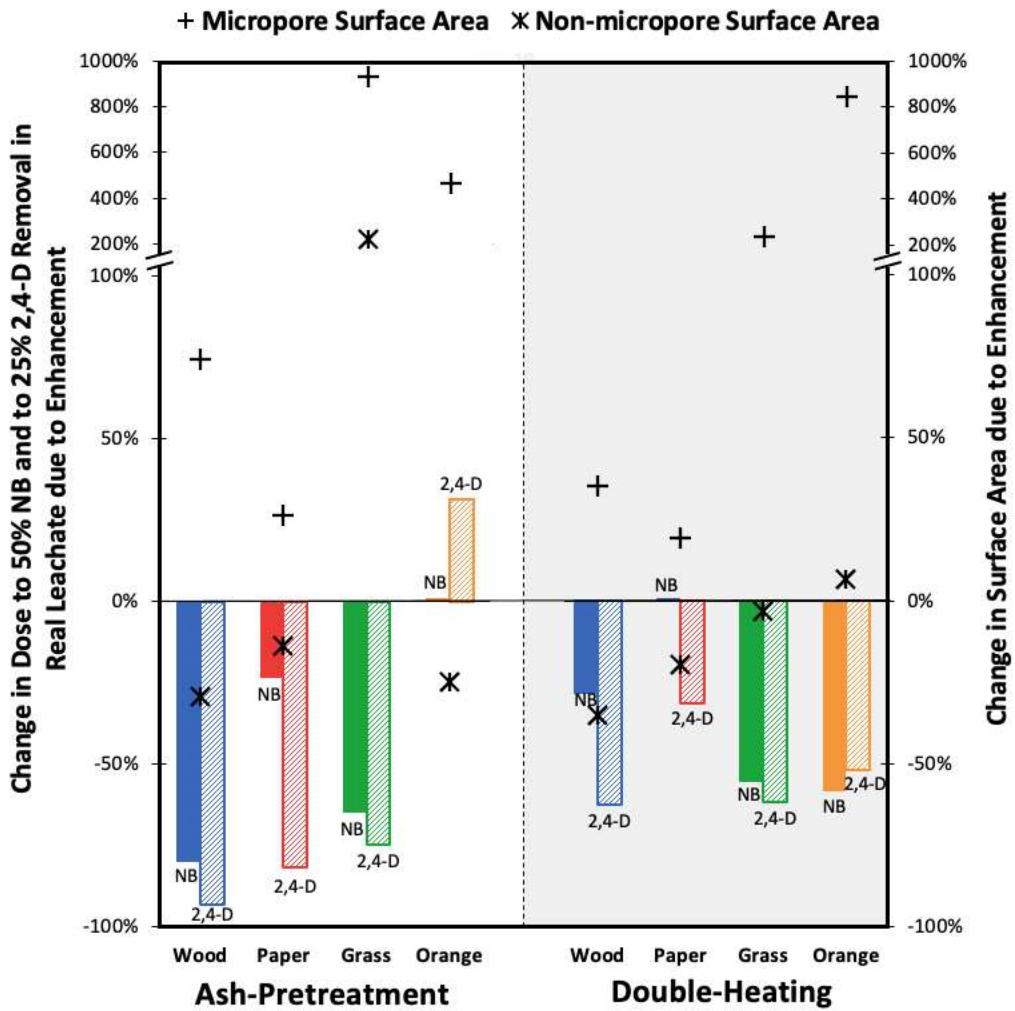
309 In addition to changing pore structure, the ash-pretreatment enhancement also changed the
310 biochar ash content (Table 1). Generally, biochar performance improved if the biochar ash content
311 increased after the enhancement (Figure S6a), but that performance improvement was not
312 correlated with the initial (feedstock) ash content (Figure S6b). For example, the low 3.2% ash
313 orange feedstock resulted in an ash-pretreated biochar that had no performance improvement in
314 real leachate and only a slight improvement in synthetic leachate. Alternatively, the high 18% ash
315 paper feedstock resulted in an enhanced biochar with a sorption capacity that was up to 5.5 times
316 better than the non-enhanced biochar; so, some high ash feedstocks may still benefit from an ash-
317 pretreatment enhancement.

318 Given the promising performance improvements, biochar enhancements could help
319 narrow and improve the performance range of biochars produced from OFMSW. This is especially
320 important since OFMSW is heterogeneous and variable. However, due to the inconsistent trends
321 and limited data, a better understanding of the enhancement methods' mechanisms is needed. This
322 is especially important because different enhancements are needed to help biochar overcome the
323 significant, negative impacts from leachate DOM. Future research could support developing
324 further enhancements to OFMSW biochars that achieve more consistent and larger improvements.

325 Overall, this study can provide the basis for a novel organics diversion approach through
326 OFMSW biochar production that reduces climate change impacts, harvests energy from waste,
327 and reduces landfill air emissions, and that could incentivize enhanced leachate treatment. By
328 producing biochar from a diverse set of materials that captured the main categories of OFMSW
329 and under constant pyrolysis conditions, this study provides a baseline dataset to (i) support the
330 selection of OFMSW components expected to produce the most efficient biochar adsorbent; (ii)
331 validate the use of biochar enhancement techniques to improve waste-derived biochar sorption
332 performance in landfill leachate for a large range of OFMSW components; and (iii) understand the
333 impact of landfill leachate DOM impact on biochar performance. Future research can build upon
334 this work by evaluating more feedstocks and enhancement approaches as well as potential
335 correlations between feedstock characteristics and biochar performance.

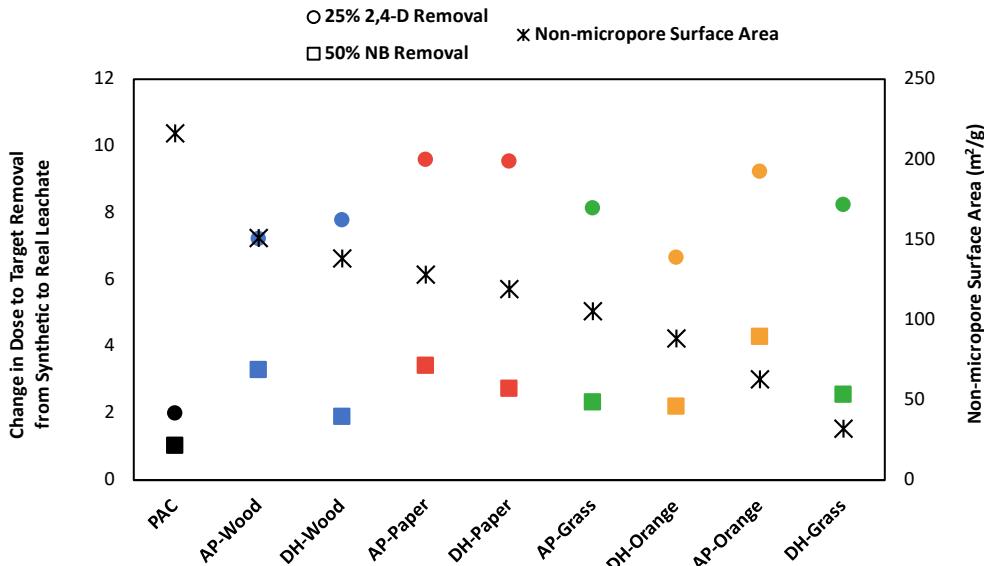
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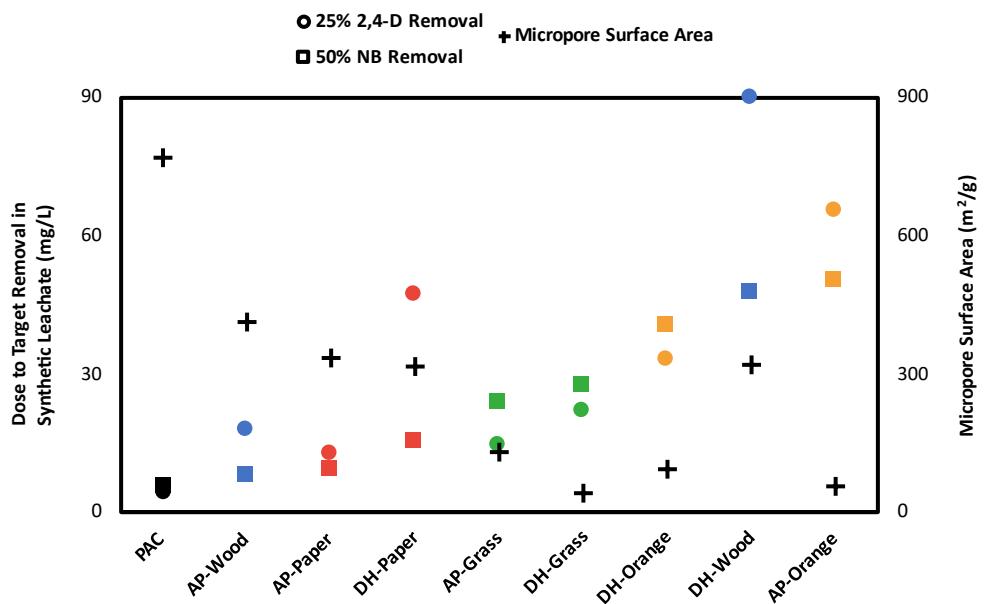


338
339

340 **Figure 2.** Impact of the ash-pretreatment and double-heating enhancements on biochar
341 performance and pore structure; there was no correlation between type (increase or decrease) or
342 magnitude of changes between each respective enhanced and non-enhanced biochar pair. Left axis
343 (columns) show changes to biochar performance in real leachate (solid columns for 50%
344 nitrobenzene (NB) removal; hashed columns for 25% 2,4-D removal); a negative percent dose
345 change represents an improvement to biochar performance (i.e., lower dose required) due to the
346 enhancement. Right axis (markers) shows changes to biochar micropore (plus sign) and non-
347 micropore (star) surface areas; note the broken axis and updated linear scale spacing for the five
348 largest surface area percent changes.
349



350
351 **Figure 3.** Factor change in dose to 25% 2,4-D and to 50% nitrobenzene (NB) removal required
352 from synthetic to real leachate background matrices; the change in dose between matrices allows
353 for the evaluation of DOM impacts. Horizontal axis (adsorbents) is ordered by decreasing non-
354 micropore surface area. The dose increase and amount of non-micropore surface area were not
355 correlated across the biochars, indicating that the non-micropore surface area was not the dominant
356 factor in accommodating the real leachate's DOM.



357
358 **Figure 4.** Biochar performance in synthetic leachate related to the amount of biochar micropore
359 surface area. Horizontal axis (adsorbents) is ordered by increasing dose to 50% NB Removal.
360 Synthetic leachate, which had had minimal DOM competitive effects, minimized the potential
361 impact of leachate DOM such that the impact of micropore surface area on adsorption capacity
362 could be better evaluated. The biochar doses to 25% 2,4-D removal and to 50% nitrobenzene (NB)
363 removal in synthetic leachate generally increased with lower micropore surface areas.

364 **Conflicts of Interest**

365 There are no conflicts to declare.

366 **Acknowledgements**

367 Removed for double blind review.

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