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Journal:	*Environmental Science: Water Research & Technology*
Manuscript ID	EW-ART-06-2021-000376.R1
Article Type:	Paper

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Water Impact Statement

Transforming the organic fraction of municipal solid waste into biochar to reduce fugitive landfill emissions and control organic micropollutants during landfill leachate treatment is a novel circular economy organics diversion approach that reduces climate change impacts and harvests energy from waste. This study incentivizes that organics diversion approach by providing the basis for a low-cost, enhanced leachate treatment method.

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

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†Electronic Supplementary Information (ESI) available: Further details on the methods and results are presented in supporting information. See DOI: 10.1039/x0xx00000x

Abstract

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

1 Introduction

Fugitive landfill gas emissions, which are mainly produced from the degradation of organic material,[1] have a significant contribution to climate change. For example, in the United States, landfill emissions are the third largest source of anthropogenic methane emissions.[2] To minimize the negative impacts of landfilling, the desire to divert organics from landfills is increasing (e.g., the United States has many existing and upcoming regulations[3]). As a result, several organics diversion approaches are being pursued,[4] and many try to take advantages of the opportunity to recover resources from the organic waste.[5,6] Despite those efforts, organics diversion strategies still lack widespread implementation.[7] Thus, there is a need for additional organic waste management strategies that can valorize this waste stream.

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

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

OFMSW is a complex feedstock that is comprised of four main components (food waste, 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 husk[34]) 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.

2 Methods

2.1 Feedstock and Activated Carbon Selection

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

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

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

2.2 Biochar Production and Characterization

Biochar was produced by pyrolyzing feedstocks and then grinding the resulting char, following established methods.[21,41,42] Each feedstock was packed into 450 mL covered crucibles and pyrolyzed in a muffle furnace at 850 °C for 2 hours.[21,41,43–45] This approach is representative of many full-scale pyrolysis operations, which do not conduct nitrogen purging.[46] Resulting biochars were ground with a mortar and pestle and wet-sieved to particle sizes between 38 and 75 μm (200 and 400 sieve size) and dried at 105 °C for at least 24 hours.[17] This grinding and drying was also used to produce powdered activated carbon (PAC).

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

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

2.3 Real and Synthetic Landfill Leachates

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

The synthetic leachate was modified from an established recipe[18,19] by decreasing volatile fatty acid (VFA) concentrations to a total chemical oxygen demand (COD) of 6000 mg/L and substituting the original recipe's non-VFA organic compounds with the two representative OMPs, nitrobenzene and 2,4-D. The synthetic leachate was representative of real leachate water quality with respect to most constituents including ionic strength and chemical oxygen demand but excluded the complex mixture of leachate-derived DOM matter (Table S2). The synthetic leachate was also stored in air-tight amber bottles at 4°C for up to three days prior to batch testing. The pH, UVA_{254}, and COD of the synthetic leachate did not change more than 10% over three days (e.g., pH varied by less than 4.5% and COD, measured using by less than 6.8%).

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

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

2.4 Dose Response Curves

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

2.5 Data Analysis

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

3 Results and Discussion

3.1 Evaluating Biochar Performance

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

By design, the feedstocks selected were diverse in type and chemical composition. For example, the feedstocks' measured ash contents varied from 2.0% (coffee) to 28% (peanut), measured carbon contents from 44% (grass) to 57% (coffee), and estimated cellulose contents from 18% (coffee) to 81% (paper) (Table S1). The resulting biochars also had diverse traits. For example, the biochars' composition of ash ranged from 1.2% (wood biochar) to 16% (grass biochar), O:C ratios from 3.3 (paper biochar) to 15 (grass biochar), and H:C ratios from 9.2 (paper biochar) to 21 (grass biochar) (Table 1). In particular, the biochars had a wide range of pore size distributions and surface areas. For instance, the biochar's BET surface areas spanned from 23 m^2/g (coffee biochar) to 450 m^2/g (wood biochar) and micropore surface areas from 0 m^2/g (peanut biochar) to 270 m^2/g (paper biochar) (Table 1).

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

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

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

basis. H/C represents hydrogen to carbon ratio. O/C represents oxygen to carbon ratio. Note: * 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 (m²/g)	Non-micropore Surface Area (m²/g)	BET Surface Area (m²/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

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

3.2 Improving Biochar Performance

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

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

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

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

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

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

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

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

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

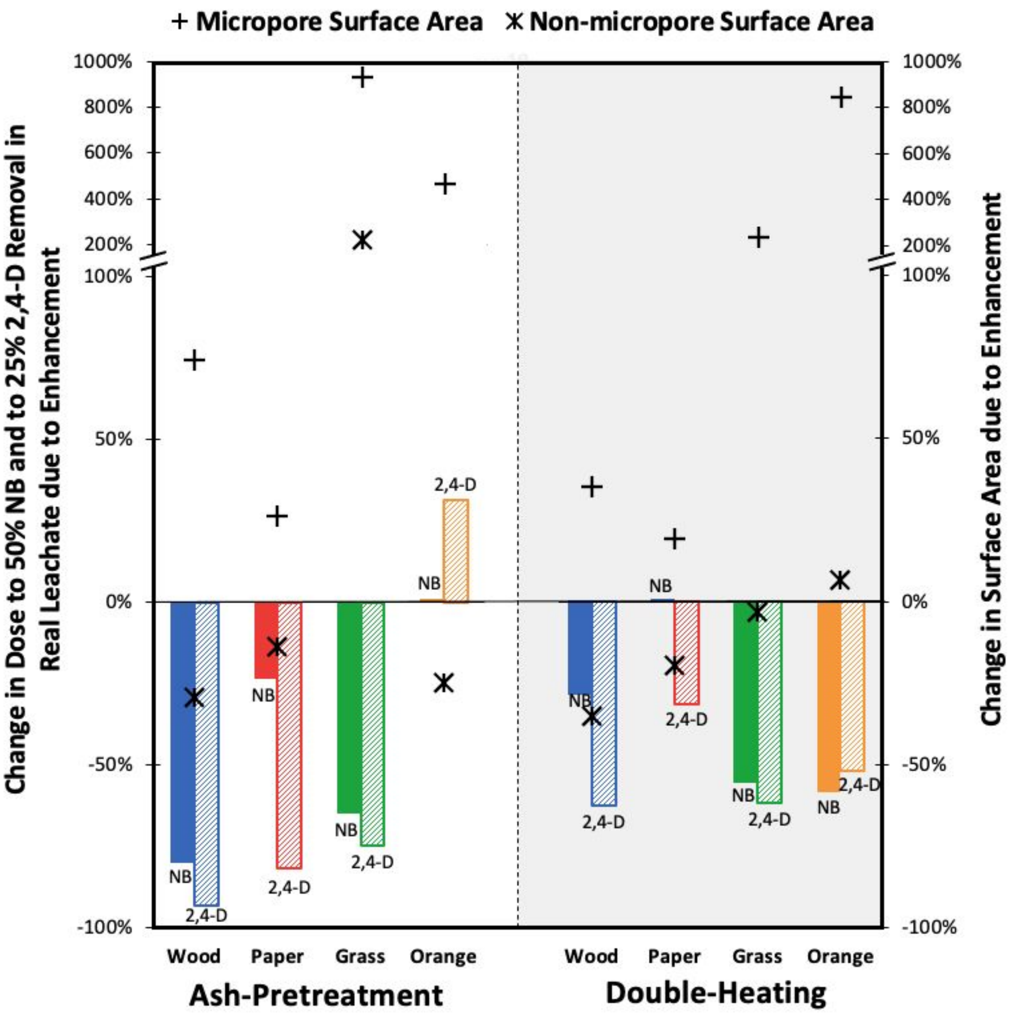

Figure 2. Impact of the ash-pretreatment and double-heating enhancements on biochar performance and pore structure; there was no correlation between type (increase or decrease) or magnitude of changes between each respective enhanced and non-enhanced biochar pair. Left axis (columns) show changes to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

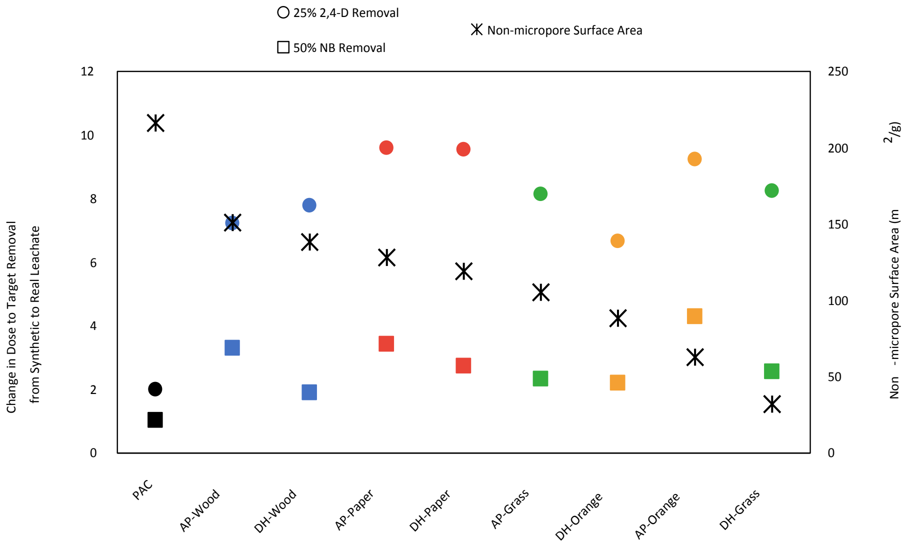

Figure 3. Factor change in dose to 25% 2,4-D and to 50% nitrobenzene (NB) removal required from synthetic to real leachate background matrices; the change in dose between matrices allows for the evaluation of DOM impacts. Horizontal axis (adsorbents) is ordered by decreasing non-micropore surface area.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

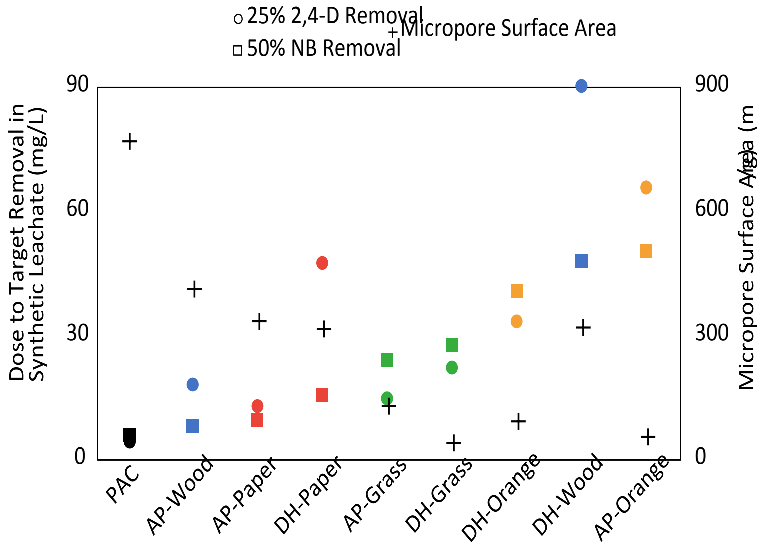

Figure 4. Biochar performance in synthetic leachate related to the amount of biochar micropore surface area. Horizontal axis (adsorbents) is ordered by increasing dose to 50% NB Removal. Synthetic leachate, which had had minimal DOM competitive effects, minimized the potential impact of leachate DOM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

Conflicts of Interest

There are no conflicts to declare.

Acknowledgements

Removed for double blind review.

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