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Ash pretreatment of pine and biosolids produces biochars with enhanced capacity for organic micropollutant removal from surface water, wastewater, and stormwater

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Abstract:

An ash pretreatment process was developed and evaluated for improving sorption of 2,4-dichlorophenoxyacetic acid (2,4-D) and sulfamethoxazole (SMX) for pine and biosolids based biochars. Pine and biosolids pellets were soaked in a dissolved ash solution and pyrolized at 800 °C. The sorption performance of untreated pine biochar, pine ash pretreated biochar, untreated biosolids biochar, biosolids ash pretreated biochar, base pretreated pine biochar, and commercial powdered activated carbon (PAC) was compared in deionized water, lake water, wastewater, and stormwater for 2,4-D and SMX removal. Dose response curves were developed at 3-hour and 7-day contact times in continuously mixed batch tests. Ash pretreatment of pine yielded over an order of magnitude increase in 2,4-D and SMX sorption compared to untreated pine biochar, making it competitive with PAC. Base pretreatment was the dominant improvement process of ash pretreatment, and the improvement from ash pretreatment was linked to the precursor feedstock inherent ash content. Adsorbent performance was strongly correlated with non-micropore (>2 nm) surface area. Background organic matter character significantly impacted sorbent performance. Ash pretreatment of biochar increased organic micropollutant sorption and is applicable in low-cost water treatment scenarios, such as stormwater and wastewater treatment, as well as in low- and middle-income countries.

Water Impact Statement

Global chemical production, use, and environmental occurrence are rapidly increasing, leading to both environmental and public health impacts. Biochar is a promising technology for addressing organic chemical pollution in drinking water, stormwater, and wastewater in low-resource settings, but its performance is limited under typical production conditions. This study evaluates a novel, low-resource biochar improvement method using ash pretreatment to improve biochar performance by an order of magnitude, making it competitive with commercial activated carbon. The ash pretreatment method described herein has potential to improve water quality and public health in resource limited and financially constrained water treatment scenarios.

I. Introduction

Expansion of chemical production, use, and disposal increases human and environmental exposure to anthropogenic organic micropollutants (OMPs) such as pesticides, pharmaceuticals, and personal care products.[1–5] Adsorption with commercial activated carbon (AC) is a prevalent technology for OMP removal from aqueous solutions, and it is often used to control OMPs in drinking water (DW) and wastewater (WW) treatment.[6–8] Because stormwater (SW) and WW are primary sources of OMPs in surface waters, water resources protection at OMP discharge sources is a key strategy for limiting public and environmental risks associated with OMPs.[9–12] Unfortunately, in many low-cost water treatment scenarios such as WW, SW, small DW systems, and low- and middle-income countries (LMICs), AC may be unavailable or too costly to implement.[13–15]

To address these limitations, use of biochar, a porous, carbonaceous material produced through biomass pyrolysis, has been investigated. Biochar is a promising alternative adsorbent to AC, as it is produced from waste biomass and maintains similar material and sorptive characteristics at much lower cost and energy requirements.[13,16,17] A wide range of feedstocks have been used to produce biochars for OMP removal in low-cost water treatment scenarios.[13,18,19] Some studies have focused on the application of biochar as a SW and tertiary WW treatment technology for the removal of nutrients and OMPs; however, biochar often has a significantly lower sorption capacity than AC, requiring larger adsorbers and more frequent replacement in typical water treatment scenarios.[16,17,20,21] Activation/improvement methods have been developed to increase biochar's sorption capacity, but most methods are expensive or impractical for large-scale biochar production, thus undermining biochar's advantages.[22,23] A low-cost, practical method that increases biochar's adsorption performance would increase its competitiveness with AC in water treatment scenarios, such as WW and urban SW treatment, as well as water treatment in LMICs.

Some biochar studies have suggested that inherent ash content in the precursor feedstock can have significant positive or negative impacts on OMP sorption, depending on the biochars' production conditions.[16,24–26] In addition, the presence of calcium, as well as other alkali and alkali-earth metals (AAEMs) present in biomass ash,[27,28] have been shown to catalyze pore development and alter surface area during pyrolysis of precursor feedstocks, as well as during reactivation of ACs.[29–33] The impact of feedstock-inherent ash content prior to pyrolysis on biochar sorption of OMPs is not well understood.[33] This study seeks to address this gap by evaluating the impact of a novel method, ash pretreatment, for improving biochar performance on biochar physicochemical characteristics and OMP sorption for pine and biosolids biochars in DW, WW, and SW treatment scenarios.

II. Materials and methods

A. Sorbent production

Pelletized pine (Confluence Energy, Kremmling, CO, USA) and dried WW biosolids (Louisville and Jefferson County Metropolitan Sewer District, Louisville, KY, USA) were selected as precursor feedstocks to span the range of typical biochar feedstock inherent ash content and chemical composition.[28] These materials were pyrolyzed at 800 ˚C to produce untreated pine biochar (PUB) and untreated biosolids biochar (BUB). After specific pretreatments on the raw feedstocks, pine ash pretreated biochar (PAB), pine ash pH-matched biochar (PAMB), biosolids ash pretreated biochar (BAB), and biosolids ash pretreated biochar – concentrated (BAB-C) were produced under the same pyrolytic conditions. These biochars were compared to a commercially available bituminous coal-based granular activated carbon (Cabot

Norit 1240), which, when ground between 200 and 400 standard mesh sizes (35 – 75 micron), is designated powdered activated carbon (PAC) herein.

To produce ash for ash pretreatment, pine and biosolids pellets were separately heated in a muffle furnace at 550 ºC for six hours. Ash leachates were prepared by mixing 2 grams of ash in 1 liter of DI water for PAB and BAB and in 0.26 liters of DI water for BAB-C – corresponding with the water absorption capacity of 200 grams of pelletized biosolids – with a stir bar in water for 30 minutes. This mixture was filtered through a 1.2-micron glass microfiber filter to remove remaining ash solids. These solutions were characterized by ICP-MS and the results are listed in Table S1. Pine and biosolids pellets were then soaked in the corresponding ash leachate at a 100:1 mass ratio of feedstock to dry ash for 12 hours. PAMB was prepared by soaking pine pellets in a pH 11 NaOH solution, matching the pH of the pine ash leachate. The pH of the biosolids ash leachate was 9. The soaked feedstocks were then dried at 110 ˚C overnight.

The raw and pretreated pine and biosolids feedstocks were then placed in oxygen-limited covered crucibles in a muffle furnace for pyrolysis at 800 ˚C for two hours. After cooling, all adsorbents were ground with mortar and pestle, washed, wet-sieved with reverse osmosis water between a 200 and 400 standard mesh (35 and 75 micron), and dried to produce the powdered adsorbents used in batch tests.

B. Sorbent characterization

BET surface area and pore size distributions were determined from Quantachrome Autosorb 1 N_2 gas sorption results using the T-plot method, which separates surface area in micropores (<2 nm width) from that in non-micropores. The pH of the point of zero charge (pH_{PZC}) was determined using an indirect titration method.[34] C, H, and N content of biochars were measured with a Perkin Elmer 2400 CHNS Analyzer. Ash content was calculated by measuring the mass remaining after heating feedstocks and adsorbents at 550 ˚C for six hours uncovered in a muffle furnace. Oxygen content was calculated as the mass percentage remaining after considering C, H, N, and ash. Physical characterization results for the adsorbents are provided in Table 2.

C. Sorbate selection and measurement

2,4-dichlorophenoxyacetic acid (2,4-D) and sulfamethoxazole (SMX) were used as target OMPs because they are very weakly adsorbing compounds, yielding results that are conservative relative to most other OMPs.[35] The target initial concentrations of 2,4-D and SMX were 200 ng/L in all waters tested, corresponding to environmentally relevant concentrations.[36,37] Tritium labeled 2,4-D and carbon-14 labeled SMX (American Radiolabeled Chemicals, Inc.) were quantified using liquid scintillation counting (Beckman LS 5000); this method was used because of the low cost of analysis, fast analysis time and low detection limit. Each sample vial included 4 mL of sample with 10 mL of Ultima Gold™ scintillation cocktail. For all background matrices, a calibration curve was developed with known concentrations of radiolabeled 2,4-D and SMX ranging from 0 to 200 ng/L. The detection limit was 4 ng/L for 2,4-D and 30 ng/L for SMX, corresponding to 98% removal and 85% removal for 2,4-D and SMX, respectively.

D. Waters

To evaluate the impact of background organic matter on 2,4-D and SMX sorption, batch experiments were conducted with four waters: deionized water (DI) phosphate buffered to pH 7.8, water with natural organic matter from Big Elk Meadows (BEM) alpine lake, secondary-treated wastewater (WW), and mixed snowmelt stormwater collected from a storm drain in Boulder, CO (SW). These four waters represent a wide range of background organic matter character. pH was stable for all waters throughout the sorption process (<0.1 pH change). The dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UVA_{254}), and specific ultraviolet absorbance (SUVA) values are shown in Table 1. BEM at DOC concentrations of 2, 4.5, and 8 mg/L was prepared from a concentrate. BEM at 2 and 8 mg/L was used to evaluate the impact of initial background organic matter. All other BEM was diluted to 4.5 mg/L DOC as listed in Table 1.

Table 1 Background matrix characteristics

Water	DOC mg/L	UVA_{254} cm^{-1}	SUVA L/mg-m	pH
DI	< 0.1	-	-	7.8
BEM	4.5	0.108	2.4	7.9
WW	6.7	0.113	1.7	7.6
SW	7.6	0.114	1.5	7.7

E. Batch experiments

Batch sorption experiments were conducted in duplicate 40 mL amber vials filled with the target compound spiked water, to which biochars were dosed from biochar/DI water slurries of 0.1, 1, 10, and 20 g/L concentrations using pipets to improve accuracy of biochar dosing at low concentrations.[16] The overall dose range, 0.1 to 5000 mg/L, was specified by the sorption capacity. The dosed vials were immediately transferred to a 13 RPM rotary mixer for 3 hour and 7 day contact times before being filtered through a 1.2 micron glass microfiber filter and analyzed by liquid scintillation counting. Fitting the batch data with standard isotherm models, e.g., Freundlich or Langmuir, did not account for the adsorption competition by the background organic matter, thus dose response curves were utilized.[38] The doses required to achieve 25% and 75% removal of 2,4-D and SMX were calculated by interpolation between the two closest points on each dose response curve. Where 25% or 75% removal was not met due to the high sorbent dose required, the dose required is indicated as greater than the maximum dose tested. The overall average absolute difference between duplicates' percent removal was 2.7% (n=1,848).

An initial kinetic test at a single sorbent dose was performed for PAC, PAB, and PUB at 0.5-, 1-, 3-, 6-, 24-hour, 7-day, and 14-day contact times to establish an adequate contact time for sorbent comparison. For the initial kinetic tests, adsorbent doses for PAC, PAB, and PUB were selected to achieve the same ultimate removal at 14 days, corresponding to a dose of 2.5, 10, and 100 mg/L, respectively. 2,4-D and SMX removal in the kinetic test were then normalized to the 14-day removal in order to compare the kinetic performance of the materials. For 2,4-D and SMX removal with biochar (PUB and PAB) and PAC, a 3-hour contact time was found to be sufficient to differentiate and rank the kinetic performance of various sorbents, and the results from 7-day (168 hr) contact time approach those of the 14-day test (Figure S1). Results reported, unless otherwise specified, are for the 3-hour contact time, which captures the kinetic performance of the adsorbents that would be relevant in powdered adsorbent applications, such as in a DW or WW treatment plant.[16] Dose response curves were developed for all sorbents in DI and all background matrices at 3-hour and 7-day contact times, and 2,4-D and SMX removals were related to UVA_{254} removal in order to evaluate the predictive power of UVA_{254} for OMP removal in DW, SW, and WW.

III. Results and discussion

A. Adsorbent characterization

The sorbent physical and chemical characteristics varied considerably based on precursor feedstock and applied pretreatments (Table 2). The pine feedstock (0.4% ash) and pine biochars had lower ash and higher carbon content than did the biosolids feedstock (20% ash) and biosolids biochars. In addition, the BET surface area, micropore (< 2 nm width) surface area, and micropore fraction were much higher for the pine biochars compared to the biosolids biochars, suggesting that precursor feedstock is an essential consideration for biochar adsorption studies.[16] The pine biochars had about half the BET and micropore surface areas compared to the PAC, but a similar micropore surface area fraction ~80-90%.

Table 2 Physical characterization of adsorbents. Pine and biosolids raw ash content are 0.4% and 20% respectively.

Material	C	O	H	N	Ash	BET Surface Area m^2/g	Micropore Surface Area		Non-Micropore Surface Area		pH_{PZC}
	%	%	%	%	%		m^2/g	%	m^2/g	%	
Powdered Activated Carbon (PAC)	79	14	0.37	0.43	6.8	1080	850	79	230	21	9.7
Ash Pretreated Pine Biochar (PAB)	85	12	0.70	0.19	2.8	510	420	82	90	18	9.0
Pine-Ash pH-Matched Biochar (PAMB)	86	11	0.71	0.13	1.8	443	370	84	73	16	8.1
Untreated Pine Biochar (PUB)	90	6.9	0.67	0.22	1.7	424	380	90	44	10	9.0
Ash Pretreated Biosolids Biochar – Concentrated (BAB-C)	40	2.0	0.72	3.5	54	30	7	23	23	77	7.9
Untreated Biosolids Biochar (BUB)	38	5.7	0.71	3.1	53	46	19	41	27	59	7.4
Ash Pretreated Biosolids Biochar (BAB)	31	6.7	0.25	2.2	60	76	42	55	35	45	8.4

Ash pretreatment increased the ash content of pine biochar by 50% and biosolids biochar by 2-10%, indicating that inorganic uptake is occurring through the pretreatment process.[27] The base pretreatment, however, had an insignificant effect on the ash content of pine. Both ash and base pretreatment raised the oxygen content and slightly lowered the carbon content of the pine biochars, indicating slightly higher hydrophilicity (by increasing the H:C ratio by 10%) and increased surface functional groups (by increasing O:C ratio by 90% and 70% respectively).[16] Ash pretreatment did not change the pH_{PZC} of pine, but base pretreatment slightly lowered it.

While ash and base pretreatments increased the BET surface area of pine biochar by 20% and 5%, respectively, the percentage of micropores in PAB and PAMB decreased, indicating a shift toward pores larger than 2 nm (non-micropore surface area). Ash and base pretreatment increased non-micropore surface area by 105% and 66%, respectively. This is likely due the pre-pyrolysis addition of base and metals, which have been shown to catalyze biomass decomposition reactions[39] and increase pore development and pore size of carbonaceous adsorbents through intercalation[39–41] and gasification reactions.[29,42]

Ash pretreatment of biosolids showed smaller relative changes in ash content, chemical composition, surface area, and pore size distribution compared to pine biochars. For biosolids biochars, it is likely that the high inherent ash content in the feedstock reduced the impact of ash pretreatment, and the high amount of ash could be causing over-catalyzation of the material, leading to the lower BET surface area observed for BAB-C. The surface area of BAB-C was nearly all non-micropore (> 2nm) surface area, which is indicative of overcatalyzation.[31]

B. Adsorbent performance

Dose response curves for 2,4-D removal at a contact time of 3-hours for all seven sorbents in each background matrix (DI, BEM, WW, and SW) are presented in Figure 1. The estimated doses required to achieve 25% and 75% percent removal of 2,4-D and SMX are listed in Table 3. Results from the 7-day tests are shown in Table S2 and Figure S2 and exhibit the same relative adsorption behavior as the 3-hour test results.

Table 3 Dose (mg/L) to achieve 25% and 75% removal of 2,4-D and SMX for all adsorbents in DI, BEM, WW, and SW after a 3-hour contact time.

Compound	Sorbent	DI		BEM		WW		SW	
		25%	75%	25%	75%	25%	75%	25%	75%
2,4-D	PAC	3.4	22	6.4	26	14	64	21	90
	PAB	8.5	36	13	70	36	190	84	360
	PAMB	22	81	34	110	73	320	130	480
	PUB	77	330	170	590	390	1600	1000	3300
	BAB-C	160	690	310	1300	-	-	1400	4200
	BUB	230	1200	550	1800	460	1800	2300	>5000
	BAB	420	1500	510	2400	790	2800	2000	>5000
SMX	PAC	4.3	23	8.6	43	21	85	26	140
	PAB	10	48	27	88	68	330	130	470
	PAMB	31	90	60	150	120	440	230	840
	PUB	95	450	440	940	880	2800	2100	>5000
	BAB-C	330	1400	550	1300	-	-	2200	4800
	BUB	440	1500	1000	2600	1000	4400	4100	>5000
	BAB	660	2000	1500	>2300	1300	>4500	3352	>5000

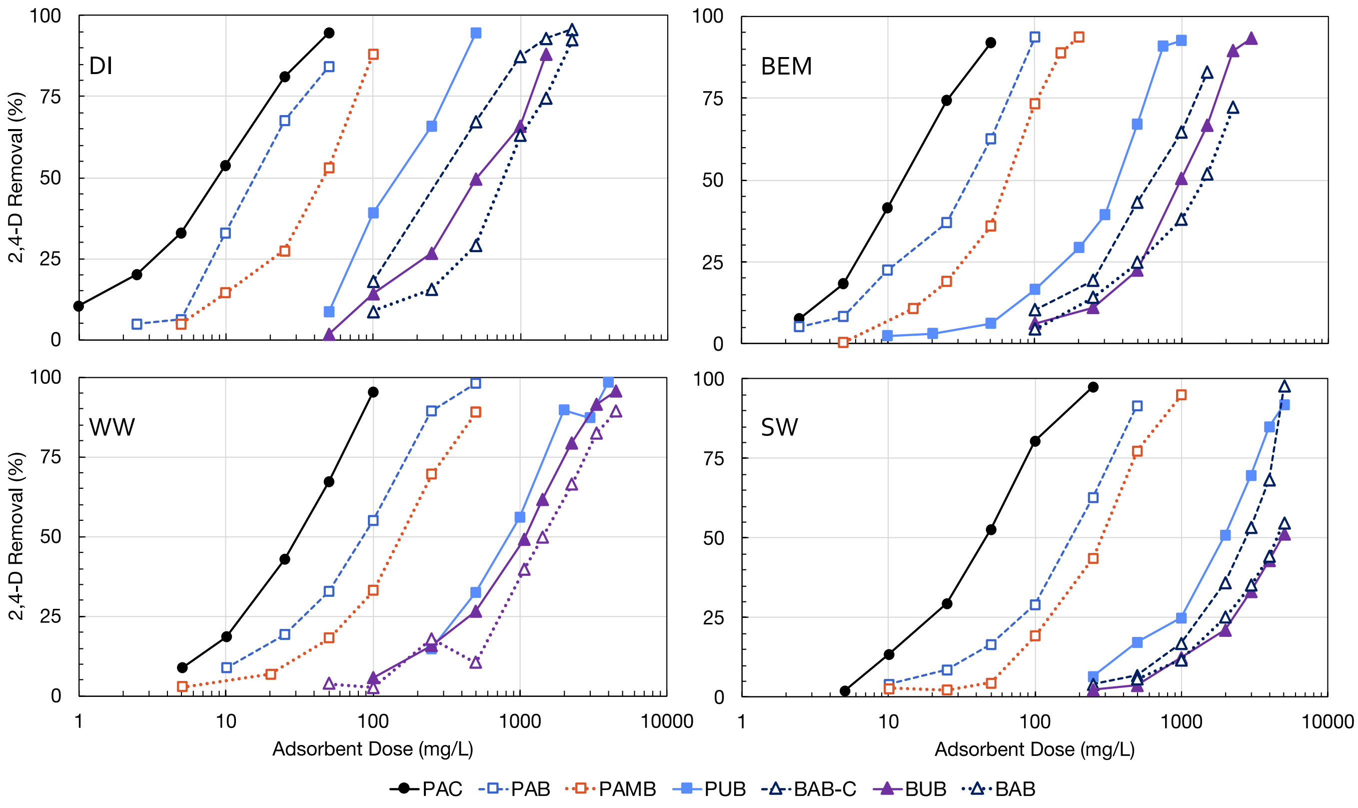

Figure 1 Dose response curves in DI, BEM, WW, and SW for removal of 2,4-D with all sorbents after a 3-hour contact time.

The same sorption capacity ranking of sorbents was evident in all four background matrices. PAC outperformed all of the biochars, and the biochars were grouped in two performance categories. The lower-performing biochars were the untreated pine biochar, PUB, and all biosolids-based biochars, BUB, BAB, and BAB-C; these biochars required doses around two orders of magnitude higher than PAC to equivalently remove 2,4-D and SMX. However, the two higher-performing biochars, the ash pretreated pine, PAB, and the base pretreated pine, PAMB, outperformed the other biochars by around an order of magnitude. Thus, these pretreatment methods yielded biochars that are much more competitive with PAC for 2,4-D and SMX removal. PAB was the highest performing biochar, requiring only 2 to 4 times the PAC dose to achieve the same level of removal in all background matrices, while the PAMB required about 4 to 5 times the PAC dose to achieve the same removal.

BAB-C exhibited higher performance than BUB and BAB in all background matrices where it was tested, indicating the importance of concentration and water absorbing capacity of the precursor feedstock in the ash pretreatment process. BAB was indistinguishable from BUB in all background matrices, likely because the raw biosolids pellets were not able to absorb all of the biosolids ash leachate, leading to observable precipitation of metals on the surface of the biosolids and glassware during the drying process, where it was unable to catalyze pore development in the material during pyrolysis. In addition, the lower pH (pH = 9) and lower concentration of catalytic metals (Ca^{2+} excepted, Table S1) of the biosolids ash leachate should lead to decreased decomposition/catalyzation of the material prior to and during pyrolysis. The higher performance of the BAB-C was presumably because it was able to absorb all of the concentrated biosolids ash leachate solution, thereby taking up all of the base and metals into the material prior to pyrolysis.[33,43]

The ash pretreatment of pine biochar yielded significant improvement in sorption performance, while for biosolids the performance improvement was not as great nor as consistent. It is hypothesized that pine exhibited a greater improvement during ash pretreatment because of the 50% increase in biochar ash content, while the biosolids exhibited less improvement because of the lower 2-10% increase in biochar ash content. Other studies have shown ash content to have great influence during the pyrolysis process of biomass, and the interaction between inherent ash and additional ash added through ash pretreatment is likely the cause of varied levels of improvement from the ash pretreatment process when comparing raw pine and biosolids.[33,44,45]

To elucidate insights into the improved performance observed for ash pretreated pine, the performance of PAB and PAMB were compared, since PAMB isolates the base pretreatment effect originating from the high initial pH of the ash soaking solution (pH=11). Both PAB and PAMB required significantly lower adsorbent doses when compared to PUB, suggesting the importance of the base pretreatment component of the ash pretreatment process. Base addition alone, PAMB, improved performance by 5 to 9 times compared to untreated pine, PUB, but the pH-matched biochar was unable to account for all of the improvement observed through ash pretreatment, PAB, which performed 8 to 19 times better than PUB. The positive impact of base pretreatment on adsorbent performance is supported by other studies showing that base addition, as a pretreatment, improved adsorption performance of biochars and activated carbons by increasing surface area and pore size.[33,43,46–50] The results of this study suggest that base pretreatment dominates improvement in performance for ash pretreated biochars.

Because base pretreatment cannot account for all of the improved performance observed for PAB, another process – alkali and alkali-earth metal (AAEM) catalysis – is believed to further increase the ash pretreated biochars' performance. AAEM presence and addition to raw biomass prior to pyrolysis has been shown to influence biomass thermal degradation, and some of the metals present at high concentrations in the ash leachates (Table S1) are catalytic in pyrolysis processes.[32,33,41] Metal catalysis during pyrolysis has been shown to generate micropores and expand the size of micropores through gasification and intercalation reactions, which could explain the additional improvement in performance between PAB and PAMB.[33,41,43] This hypothesis is supported by both the higher micropore (<2 nm) and non-micropore (>2nm) surface area of PAB compared to PAMB (Table 2).

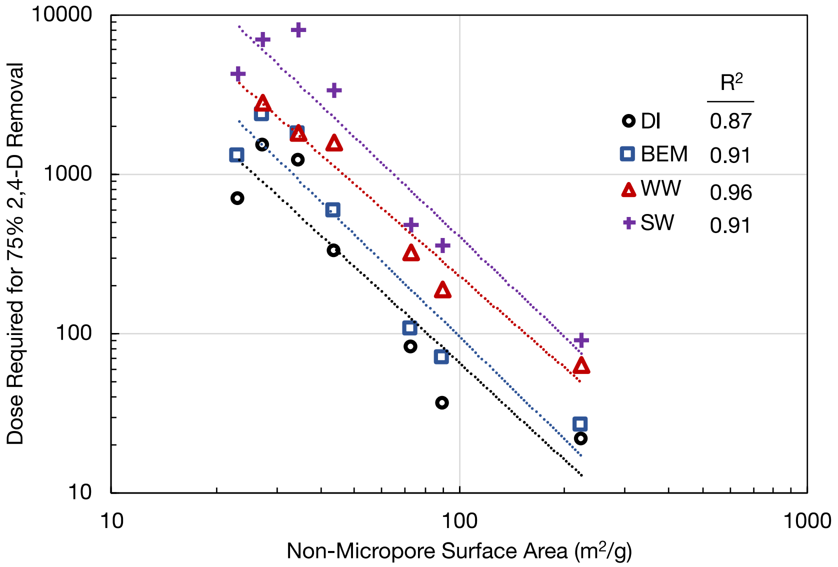

Figure 2 Dose required for 75% removal of 2,4-D for 3-hour contact time correlated with non-micropore surface area in DI, BEM, WW, and SW for all six biochars and PAC (see Table 1).

C. Impact of adsorbent physicochemical properties

Correlations were developed between dose required for 75% removal of 2,4-D and BET surface area, as well as the micropore and non-micropore fractions of the BET surface area (Table 1), as shown in Figure S3. Non-micropore surface area was strongly correlated with performance (adsorbent dose to 75% removal) in all background matrices, as shown in Figure 2, while total BET and micropore surface area were not, which is similar to what others have reported.[51] An increase in non-micropore surface area from about 25 m^2/g to 200 m^2/g yielded a decrease in the dose required for 75% removal by nearly two orders of magnitude in all background matrices. Of all physicochemical factors measured in this study, only non-micropore surface area could account for performance of both pine and biosolids biochars, PAC, and all pretreatment methods. This result indicates that non-micropore surface area – as measured by the

T-plot method – could prove a valuable measure for screening biochars for use as powdered adsorbents in water treatment scenarios. Future studies should evaluate the viability of non-micropore surface area to predict performance across a wider range of biochar feedstocks and OMPs.

Ash and base pretreatment caused primarily an increase in non-microporous surface area (Table 2) by 105% and 66% respectively, which best explains their improved performance. This increase in non-micropore surface area is likely due to base and AAEM catalysis of biomass, which have both been shown to widen micropores and increase mesoporosity, increasing the surface area that is accessible to organic micropollutants.[32,33] Correlations between other physicochemical factors (chemical composition, H:C, O:C, pH_{PZC}, etc.) of the 7 adsorbents and performance were not significant.

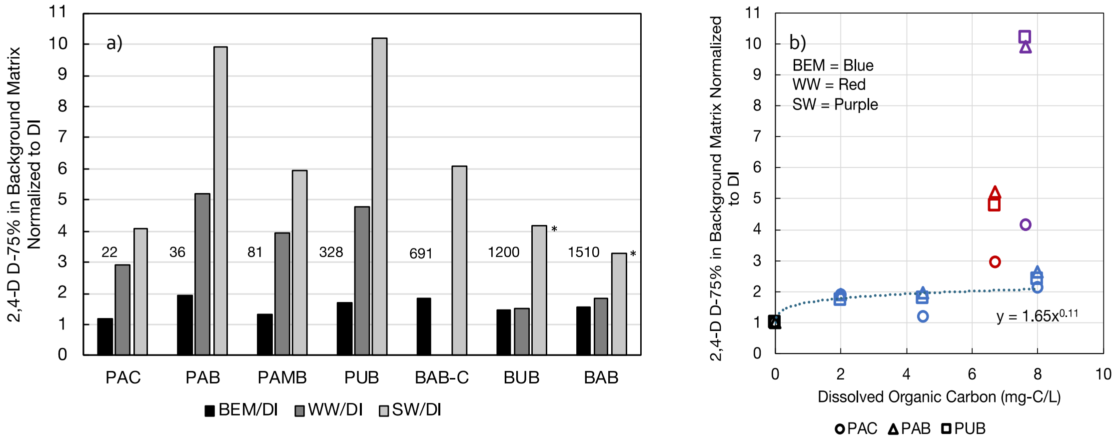

Figure 3 Normalized dose required to achieve 75% removal (D-75%) of 2,4-D in BEM (TOC = 4.5 mg/L), WW (TOC = 6.7 mg/L, and SW (TOC = 7.6 mg/l) normalized to that in DI for all adsorbents. a) Values listed above bars denote dose, mg/L, required in DI. (* denotes maximum dose did not reach 75% removal, and corresponding bars are calculated using maximum dose tested) b) impact of DOC concentration in BEM (DOC = 2, 4.5, and 8 mg/L) and

DOC character between BEM, WW (DOC = 6.7 mg/L), and SW (DOC = 7.6 mg/L) on PAC, PAB, and PUB.

D. Impact of the background matrix

The performance of all adsorbents was negatively impacted by the presence of dissolved organic matter (DOM), as higher doses were required to achieve 25% and 75% removal in all background matrices, increasing from DI to BEM, WW, and SW. This is shown in Figure 3a, where the sorbent dose in each background matrix is normalized to that in DI. The ash pretreatment process, PAB, while increasing the performance by an order of magnitude, did not reduce the relative impact of background OM competition compared to untreated pine biochar, PUB. Base pretreatment of pine, PAMB, however, did slightly reduce the relative impact of OM competition.

The relative impact of the background matrix on OMP sorption was feedstock and pretreatment dependent, indicating that adsorbent characteristics influence the magnitude of competition between the target micropollutants and background DOM (Figure 3a). Of the higher-performing adsorbents at the 3-hour contact time, PAC was least-impacted by the background matrix, followed by PAMB, followed by PAB and PUB, which were impacted similarly. For these adsorbents, the dose required to achieve 75% removal in the background matrix relative to the dose required in DI was 1-2x for BEM, 3-5x for WW, and 4-10x in SW. The lower-performing biosolids biochars were impacted similarly by the background matrices, with BEM and WW performing similarly, and SW requiring around 6x the dose required in DI water for 75% removal of 2,4-D and SMX. These results indicate that background matrix impacts must be considered for adsorbents using conditions as similar to the treatment scenario as possible, because the performance is dependent on the feedstock, production methods, background matrix, and contact time.

In some treated drinking waters, DOC concentration has been shown to be a good predictor for adsorption of organic micropollutants.[52,53] This was the case for PUB, PAB, and PAC in BEM, a DOM representative of unimpacted drinking water sources, as shown in Figure 3b. The relative background matrix impact was independent of sorbent type in the DOC concentration range 2 to 8 mg/L in BEM, shown by the correlation between DOC and background matrix impact across the three adsorbents. However, the character of the WW and SW background matrices negatively impacted the performance more than would be predicted by the correlation developed for BEM. This indicates that the character of the background matrix is more significant than the magnitude of the DOC across these background matrices.

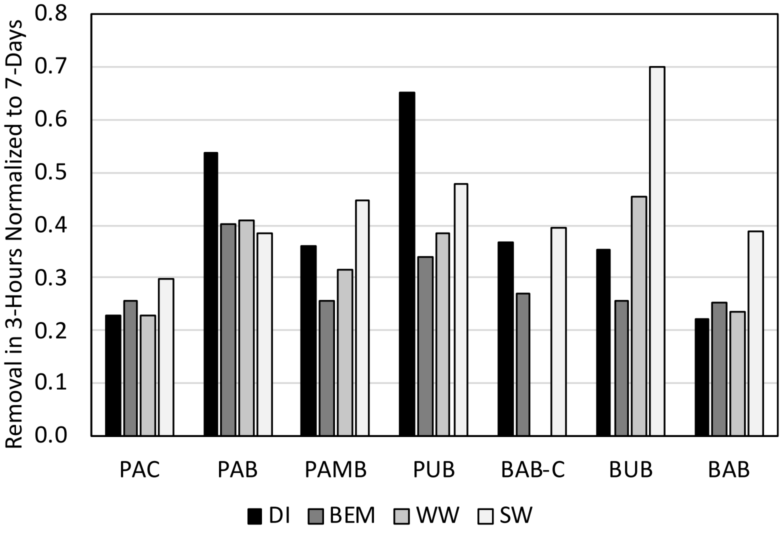

Figure 4 Removal of 2,4-D at 3 hours normalized to removal at 7 days in all background matrices

E. Kinetic performance of adsorbents

Understanding the kinetic performance of adsorbents is important for many practical water treatment scenarios, such as the application of powdered adsorbents (e.g., PAC), in non-plug flow reactors. PAC is often added as a slurry to control taste and odor or remove micropollutants during episodic events at water treatment plants, and adsorbent kinetics are important in these applications where contact time is limited and adsorption capacity is not exhausted.

The 2,4-D removal in 3-hour tests relative to removal in 7-day tests is shown in Figure 4. PAC, while the highest performing adsorbent (Figure 1), shows the lowest relative removal in 3-hour tests, indicative of slower kinetics. Of the three higher performing pine biochars, PAB and PUB displayed the fastest kinetics, achieving 40-50% of the 7-day removal in the first 3 hours, compared to 25% for PAC. Base pretreatment, while improving capacity, reduced the relative kinetics of the pine biochar to ~35%. This could be due to an increase in surface area without increasing pore connectivity or mesopore surface area, which have been shown to increase rate of micropollutant sorption.[54,55]

While biochars were more negatively impacted by background OM in WW and SW in the 3-hour contact times, PAC was more negatively impacted in the 7-day sorption tests (Figure S4). In the 7-day tests, the relative dose required for PAC was the highest, followed by PUB and PAB, suggesting that the mechanism and/or extent of adsorbent fouling changes based on contact time. 7-day contact times allow for both direct competition and pore blockage fouling mechanisms, while 3-hour tests allow for primarily the direct competition fouling mechanism.[56] These results suggest that the PUB and PAB exhibit higher direct competitive fouling, but reduced pore blockage fouling compared to PAC in terms of ultimate removal.

F. UVA_{254} as a surrogate for micropollutant removal

In order to predict and track adsorbent performance in various water treatment scenarios, UVA_{254} has been studied as a potential surrogate for micropollutant removal.[57–59] For 2,4-D and SMX removal in BEM, WW, and SW, the UVA_{254} removal was both biochar and background matrix dependent, as shown in Figure S5. General trends between UVA_{254} and micropollutant removal are weak when considering all biochars and PAC together across background matrices (Figure S5a); however, removing the weakly adsorbing biosolids biochars and evaluating each background matrix separately (Figure S5b) produced good correlations between UVA_{254} and micropollutant removal for the remaining four adsorbents ($R^2>0.8$ for WW and SW, and $R^2>0.6$ for BEM). In nearly all cases, the 2,4-D and SMX removal was at least 15 to 25% greater than the UVA_{254} removal, thus making UVA_{254} a good conservative surrogate for 2,4-D and SMX removal for PAC and pine biochars.

The biosolids biochars, compared to the pine biochars and PAC, removed less 2,4-D and SMX at a given UVA_{254} removal, likely due to a lower surface area in pore ranges relevant for micropollutant sorption compared to the pine biochars and PAC. This finding supports the importance of feedstock selection in biochar water treatment applications.

Because each background matrix has different mixes of hydrophobic, hydrophilic, large, and small DOM, correlations for one background matrix often can't be used to predict performance in other background matrices. The strong UVA_{254} correlations for all pine biochars and PAC in a single background matrix (Figure S5b) suggest that once a relationship has been developed for an adsorbent in a target background matrix, it can then be used to predict micropollutant removal for long-term monitoring in DW and WW treatment plants as long as the source water quality is reasonably consistent over time.

G. Compound-specific differences

Across all biochars and all background matrices, 2,4-D was slightly more strongly sorbed than SMX, and all impacts for 2,4-D from background matrices, biochar pretreatments, and contact time are similarly represented in the removal of SMX. This is likely due to the physicochemical similarities between 2,4-D and SMX. 2,4-D and SMX are similar in size and should be able to access similar fractions of surface area on each adsorbent due to size exclusion effects.[51] In addition, both 2,4-D and SMX are negatively charged at the target pH, so electrostatic interactions should be similar for both compounds. Despite this, SMX was more impacted by the presence of a background matrix than 2,4-D across all background matrices and adsorbents, as shown in Figure S6a. This is most likely due to the lower log K_{ow} value for SMX, which would make it more susceptible than 2,4-D to competition with background OM. There was not a significant difference in the sorption kinetics of 2,4-D and SMX in the presence of a background matrix, indicating that competition and fouling effects were not time-dependent (Figure S6b). The level of improvement observed through ash and base pretreatment of pine for 2,4-D and SMX may not be the same for compounds with chemical characteristics (hydrophobicity, functional groups, size, etc.) different than that of these two compounds. Future work should assess performance differences across a wider suite of compound classes.

IV. Conclusions

This study shows that biochars can be produced that rival the efficacy of commercial activated carbon in powdered application scenarios, such as continuous flow stirred tank reactors, which are commonly used in water treatment for the control of episodic events such as spills or taste and odor occurrences in DW and OMP removal in WW. The biochars produced by the ash and base pretreatment processes described herein provide viable alternatives to commercial AC in source water protection and resource-limited treatment scenarios, as they are inexpensive, require low energy input, and are highly effective for OMP removal. In the presence of diverse background OM (DW, WW, and SW), ash and base pretreated biochar were found to be competitive with AC and greatly exceed the performance of untreated biochar. The background matrix character was found to be more important than the DOC concentration across background matrix types (DW, WW, and SW), and UVA_{254} can be used as a surrogate for OMP removal once a relationship has been established between an adsorbent and the background matrix. Non-micropore surface area was strongly correlated with performance, and ash and base pretreatments increased the non-micropore surface area of the adsorbents, thereby improving OMP sorption. Feedstock ash content is a significant factor affecting biochar performance, and future work should continue to evaluate the impacts of ash across a broader range of materials and treatment scenarios to produce high performance, appropriate adsorbents relevant for source water protection as well as water treatment in LMICs.

Conflicts of Interests: The authors have no conflicts of interests to declare.

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