

NWRI GRADUATE FELLOW SEMI-ANNUAL PROGRESS REPORT

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Project Title: Biochar Sorbents for the Control of Organic Contaminants:
Understanding Biochar Structure and Water Quality on Sorption Behavior

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Background

Controlling organic contaminants (OCs) will be a key challenge for wastewater and stormwater reuse because of public concern over the presence of OCs in water and increasingly stringent OC regulations. As inexpensive energy resources are depleted, standard technologies used to control OCs such as reverse osmosis and advanced oxidation processes may become more expensive as they require significant energy inputs to operate. Thus, a low-cost, sustainable technology that can remove OCs for wastewater and stormwater reuse is needed.

Biochar is a sorbent generated from the pyrolysis of biomass that can exhibit comparable OC sorption capacities to activated carbon¹⁻⁴, and can be produced for less than one-sixth of the cost of activated carbon.⁵ Based on a life-cycle assessment, we showed that biochar is more environmentally friendly than activated carbon to control OCs for tertiary wastewater treatment.⁶ Although biochar has the potential to be widely used to remove OCs in water reuse applications, a better understanding of the relationship between its production conditions and sorption behavior is needed.

Biochar sorption behavior such as sorption-desorption kinetics and interactions with background dissolved organic matter (DOM) are determined by its physicochemical properties (e.g., surface area, pore size distribution, surface functional groups). These properties vary with production conditions (e.g., peak temperature, pyrolysis duration).¹⁻⁴ While a few studies have investigated the influence of production conditions on biochar characteristics and associated sorption behavior, most are limited to batch experiments testing equilibrium uptake in deionized water with a small set of OCs and biochars. Moreover, no published studies, to our knowledge, have investigated OC sorption and desorption under dynamic, flow-through conditions.

My proposed research plan is to elucidate how production conditions and precursor materials determine the physicochemical structure and concomitant OC removal efficiency of biochar sorbents.

Research hypotheses

Hypothesis 1: Biochar sorption capacity and mechanisms can be predicted based on the pyrolysis regime and OC properties.

Hypothesis 2: The decrease in OC sorption capacity of different biochars in the presence of DOM will depend on the DOM characteristics and sorption mechanisms.

Hypothesis 3: Sorption and desorption kinetics under flow-through conditions will vary depending on the physical properties of the biochar and OC.

Preliminary Results

Influence of temperature, feedstock, surface area, and elemental ratios

Biochar was produced from pine wood at three different temperatures at 350, 625, and 850 °C. As shown in Figure 1, as the peak temperature of pyrolysis increases, surface area increases whereas H:C and O:C ratios decrease, which is consistent with previous studies.⁷ The sulfamethoxazole sorption capacity of these biochars, as well as high-ash biochars (Ash content >70%) produced from biosolids, primary sludge, secondary sludge, dissolved air flotation thickened solids, and fecal matter produced at 850 °C, was evaluated. These experiments were conducted in DI water and the initial concentration of sulfamethoxazole was 100 ng/L. *Most notably, the biochar produced from wood and biosolids at 850 °C exhibited the same and 30% of the sorption capacity as a commercial powdered activated carbon.*

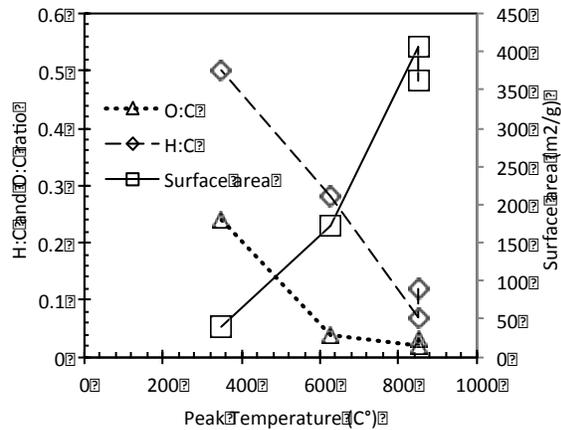


Figure 1: The relationship between peak temperature with surface area and elemental ratios.

The dose necessary to achieve 75% sulfamethoxazole removal was determined for each sorbent, minus the ash content ($^{AFM}Dose_{75\%}$), and is plotted against surface area of the sorbent, minus any contribution of surface area from the ash (Figure 2). The ash free matter doses and surface areas are plotted since ash was found to not exhibit any sorption capacity. As $^{AFM}Dose_{75\%}$ values decrease sorption capacity increases. Thus, sorption capacity appears to increase with surface area, but eventually plateaus, suggesting that surface area alone cannot predict biochar sorption capacity (Figure 2). $^{AFM}Dose_{75\%}$ values are also plotted against H:C and O:C ratios (Figure 3). For the low ash materials, as H:C ratios (i.e., aromaticity) increase and O:C (i.e., polarity) decrease biochar sorption capacities increase. Since peak temperature is related to each of these parameters, these results show that as peak

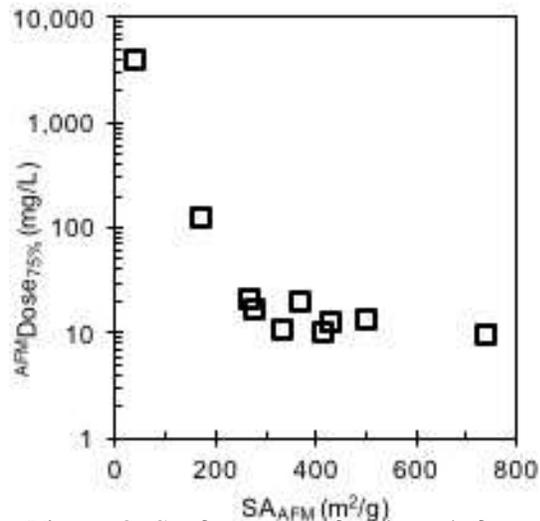


Figure 2: Surface areas for the ash free material (SA_{AFM}) plotted against the ash free matter doses need for 75% sulfamethoxazole removal ($^{AFM}Dose_{75\%}$).

temperature increases, sorption capacity might also increase because of changes in surface area, aromaticity, and polarity.

For the high-ash sorbents, which were all generated at 850 °C, no correlation was found between $^{AFM}Dose_{75\%}$ values and elemental ratios, as $Dose_{75\%}$ values remained similar even though their corresponding elemental ratios varied substantially (Figure 3). Thus, relationships between elemental ratios and biochar sorption performance are probably robust only *within* compositionally homologous feedstock classes where differences in elemental ratios arise from different production conditions and not from different precursor material properties. Therefore, future research efforts will focus on understanding the influence of production conditions and physicochemical properties on performance.

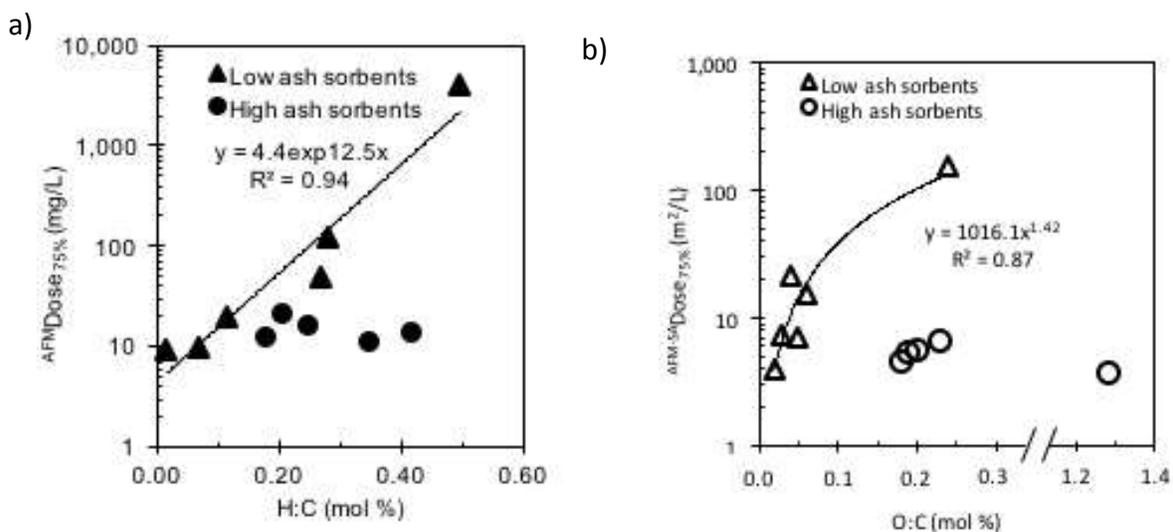


Figure 3: Ash free matter doses need for 75% sulfamethoxazole removal ($^{AFM}Dose_{75\%}$) plotted against H:C ratios (i.e., aromaticity) (a) and O:C ratios (i.e., polarity) (b).

Conclusions

These results show that biochar production conditions can be optimized to increase its sorption capacity by increasing its temperature up to 850 °C. Increasing temperature likely corresponds to improved sorption capacity due to an increase in surface area, a decrease in polarity, and an increase in aromaticity, however which parameter(s) is the most important cannot be determined based on the current data set. Since physicochemical properties vary with production conditions, relationships between biochar properties, its production, and sorption capacity can be developed. Hydrogen to carbon ratios may be the most useful as they are rapid and inexpensive to measure and could be used to screen for efficient biochar sorbents. However, such relationships may only be valid for biochars where the same or a similar feedstock (e.g., wood) is used. Biochar derived from wastewater sludge showed surprisingly high sorption capacities considering their high ash content and the fact that the isolated ash exhibited a negligible sorption capacity. These results suggest that the non-ash material in sludge biochar is very efficient at sorbing OCs, and thus biochar produced from wastewater sludge could be an efficient adsorbent.

Our results show that biochar has great potential to enable more widespread control OCs in wastewater effluent and stormwater runoff as biochar could exhibit comparable adsorption capacities of a commercial activated carbon when produced from waste materials. Since organic pollutants found in environmental waters mostly come from wastewater effluent and stormwater runoff, these low-cost sorbents could limit OC occurrence in the environment and in our water resources. Also, biochar produced from pine-beetle kill, which can be sourced from fire control efforts, and wastewater sludge, which is often landfilled or incinerated when not used as a soil amendment, could yield environmental benefits beyond making OC control more affordable while serving as a waste stream diversion method. For example, biochar production simultaneously produces energy in the form of biofuels or thermal energy, and sequesters carbon by transforming labile organic matter into a recalcitrant form.

Next steps and current research

I have generated a range of biochars by varying peak temperature, pyrolysis duration, and gaseous conditions. I am using seven different sorbates that have different functional groups to isolate the importance of different sorption mechanisms, such as hydrogen bonding and molecular sieving. The physicochemical properties (e.g., surface area, pore size distribution, aromaticity) are currently being determined using N₂ and CO₂ adsorption, and elemental analysis. I am also using these sorbents and sorbates to evaluate the impact of DOM competition from eight different sources on their performance. Future work will evaluate sorbent performance in flow-through columns.

References

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