# Raw, Torrefied, and Alkaline-treated Biomass as a Sorbent for Lead in Water

Daniel Ciolkosz,* Jennifer Desplat, and Katelyn Schiffer

Two dedicated biomass crops, shrub willow (*Salix* sp.) and miscanthus (*Miscanthus giganteus*), were evaluated for their ability to remove lead from contaminated water, both in raw ground form and after pretreatment by torrefaction or alkaline treatment. Sorption capacity experiments were conducted using a contaminant concentration that ranged from 1 mg to 15 mg per L and a biomass loading rate of 0.05 g biomass per mL. The results indicated that sorption capacities for the two feedstocks ranged from 0.15 mg to 0.26 mg of lead removed per gram of biomass, and the percentage of removal ranged from 54.3% to 93.6%. The sorption capacity of willow tended to decrease as particle size increased. Increasing torrefaction severity increased the sorption capacity of miscanthus, and alkaline treatment also increased the sorption capacity of miscanthus. The Langmuir isotherm, when fitted to measured data, characterized the samples' sorption performance with a Mean Absolute Error (MAE) of 0.0014 mmol $g^{-1}$.

*Keywords: Biomass; Sorption; Torrefaction; Alkaline; Lead*

*Contact information: Department of Agricultural and Biological Engineering, The Pennsylvania State University, 105 Agricultural Engineering Building, University Park, PA 16802 USA;*
** Corresponding author: dec109@psu.edu*

## INTRODUCTION

Lead is a common contaminant in drinking water, which is a topic of concern in the world today. Its source can be either anthropogenic, *i.e.*, lead piping or fittings in the water distribution network (Subramanin and Connor 1991; Zeitz *et al.* 2001), or geologic, *i.e.*, lead ore deposits in an aquifer (Erel *et al.* 1991; Momodu and Anyakora 2010). While activated carbon is an effective sorbent for lead removal, cost and sustainability concerns suggest that the use of biomass as a sorbent/filter medium could be a viable alternative (Volesky 1990). However, the successful implementation of this use of biomass requires an understanding of its performance for this application.

Studies have been conducted to investigate the capabilities of different varieties of biomass to adsorb heavy metals from water, including sugarcane bagasse, palm bark, eucalyptus, algae, sludge, straw, and nut shells (Pehlivan *et al.* 2009; Shokoohi *et al.* 2009; Lara *et al.* 2010; Sun *et al.* 2013; Salapa *et al.* 2018). In addition, biochar, which is biomass that has been transformed to primarily carbon *via* thermal treatment, has been studied for its capability to adsorb contaminants (Regmi *et al.* 2012; Sun *et al.* 2013; Karunanayake *et al.* 2018). Torrefied biomass, which is formed by a milder thermal treatment than is used for biochar production and hence preserves much of the molecular structure of the biomass, has also been studied to a limited degree (Salapa *et al.* 2018). Chemical modification has also been studied as a method of impacting the adsorption performance of biomass. In general, chemical treatment, usually by acids and bases, has been reported to increase sorption capacity, presumably by increasing the number of active sites for adsorption on the surface of the biomass (Romero *et al.* 2003; Ngah and Hanafiah 2007). In addition, most studies have focused on waste biomass materials (presumably due to their lower cost), with limited analysis reported on dedicated bioenergy crops.

Generally, it has been observed that both biomass and biochar are capable of adsorbing metals and other contaminants, and that the adsorption equilibrium isotherm (the relationship between the amount of contaminant adsorbed to the concentration of contaminant in the water) follows the Langmuir (Eq. 1) and/or the Freundlich (Eq. 2) isotherm, for a given sorbent material, initial contaminant concentration, and loading rate (Freundlich 1906; Langmuir 1918),

$$q_e = (q_m\, b\, C_e) / (1 + b\, C_e) \qquad \text{: Langmuir Isotherm} \qquad (1)$$

$$q_e = k_f\, C_e^{\;1/n} \qquad \text{: Freundlich Isotherm} \qquad (2)$$

where $q_e$ is the sorption uptake (mmol contaminant per g sorbent), $q_m$ is the maximum sorption uptake for a system (mmol contaminant per g sorbent), $b$ is the system coefficient, $C_e$ is the concentration of contaminant in solution at equilibrium (mmol $L^{-1}$), and $k_f$ and $n$ are the system coefficients.

The Langmuir isotherm is a chemically based model that utilizes the assumption that contaminants form a monolayer on the surface of the sorbent particles. The Freundlich isotherm is an empirical model that is readily adaptable to other situations. The use of multiple other isotherms has been proposed, each with a unique approach or application (Ho *et al.* 2001).

One of the potential mechanisms for the adsorption of lead on biomass is through interactions with polyphenolic groups, amine groups, and aromatic and aliphatic carbons, which are found in the lignin component of biomass (Taty-Costodes *et al.* 2003; Liu *et al.* 2009).

Lignin has been successfully used for the removal of heavy metal ions from aqueous effluents (Guo *et al.* 2008). Lignin has also been used as a feedstock to produce activated carbon that successfully adsorbs metal ions from contaminated water, although the morphology of lignin-based activated carbon may not be notably different than that of activated carbon from other sources (Berrima *et al.* 2016). Lignin is likely a key factor in the ability of biomass to adsorb metals (Ge and Li 2018), although cellulose and hemicelluloses can play a role as well (Pyrzyñska and Trojanowicz 1999; Hu *et al.* 2010).

Torrefaction is a mild form of pyrolysis performed at temperatures generally between 200 °C and 300 °C in an inert, oxygen-starved environment (Ciolkosz and Wallace 2011). During the process of torrefaction, hemicellulose tends to volatilize, with little or no decomposition of the hemicellulose or lignin. This means that the relative lignin content of the biomass may increase when torrefied (Tumuluru *et al.* 2011). Therefore, torrefaction may be effective at increasing sorption capacity by increasing the fraction of lignin in the solid material.

Alkaline treatment, which involves the exposure of biomass to an alkaline solution, solubilizes portions of its lignocellulosic structure, removing lignin preferentially to cellulose or hemicellulose (Silverstein *et al.* 2006). This reduction in the amount of lignin in the sample could reduce its lead sorption capacity. Alkaline reagents, such as NaOH, are also effective for the saponification of an ester group to carboxylate and alcohol (Hokkanen *et al.* 2016), which may increase the biomass particle's surface area, average pore volume, and pore diameter, counteracting the effect of reduced lignin content. Alkaline treatment can also impact a biomass sample's internal surface area, degree of polymerization, and crystallinity (Ngah and Hanafiah 2007).

While many different biomass crops exist, one attractive candidate for use in lead sorption is ground shrub willow (*Salix* spp.). This fast-growing perennial has been promoted as a biomass crop in the Northeast US and could be a reliable source of biomass for use in many applications (Wightman *et al.* 2015). Willow biomass contains 21% to 23% lignin, 38% to 44% cellulose, and 31% to 35% hemicellulose (Serapiglia *et al.* 2009, 2013). However, its sorbent properties have not yet been well-characterized.

*Miscanthus giganteus* is another biomass crop that is a candidate for sorption applications. It is a fast-growing perennial grass whose high yield, ability to grow in cold and poor soil conditions, and status as a sterile clone (thus less likely to become invasive) has made it a promising candidate for biomass production (Mishra *et al.* 2012). However, little is known about its sorbent characteristics. *Miscanthus giganteus* is made up of approximately 12% lignin, 50% cellulose, and 25% hemicellulose. As is typical of herbaceous crops, giant miscanthus' lignin content is lower than that of woody crops such as shrub willow, but it may still have promise as a sorbent for heavy metals.

Biomass crops may be more expensive to use than biomass waste, but their relatively uniform composition and the stability of their supply relative to other markets could make them a preferable feedstock for sorption applications if their sorption performance is favorable. Establishing the sorption properties of these two biomass crops would shed light on the potential for utilizing the crops for sorbent applications and would provide an additional market for the biomass. In addition to characterizing the performance of the raw biomass, it would be valuable to investigate the properties of torrefied as well as alkaline-treated samples, to help cast light on the impact of these processing steps as an additional value-added step in the preparation of biomass for use as a sorbent.

## EXPERIMENTAL

### Treatment Selection

Two species of dedicated biomass crop were selected for testing: shrub willow ("Fabius") and giant miscanthus (*M. giganteus*). For these two feedstocks, the impact of particle size, thermal treatment (torrefaction), alkaline treatment, and contaminant concentration on sorption capacity (mg Pb per dry g feedstock) was investigated. Table 1 outlines the conditions selected for the tests. Each treatment was tested in triplicate.

**Table 1.** Treatment Variables for Study

| Variable Tested | Feedstock | Particle Size (mm) | Torrefaction Temperature (°C) | Alkaline Treatment (g $L^{-1}$) | Lead Concentration (mg $L^{-1}$) |
|---|---|---|---|---|---|
| Particle size distribution | Shrub willow, Miscanthus | 3, 6, or 12 | None | None | 15 |
| Torrefaction severity | Shrub willow, Miscanthus | 6 | None, 200, 220, or 240 | None | 15 |
| Alkaline treatment | Shrub willow, Miscanthus | 6 | None | None or 0.01 | 15 |
| Contaminant concentration | Shrub willow, Miscanthus | 6 | None | None | 1, 6, or 15 |

The range of lead concentrations used in this study (1.0 mg to 15 mg Pb per L) were chosen to be within the range of those found in the field, albeit at the higher range of measured values (Adelekan and Abegunde 1992; Lee *et al.* 2005; Buragohain *et al.* 2010). In addition to the variables shown in Table 1, the sorption capacity of the two feedstocks was compared by means of a paired t-test of all data in which both feedstocks were utilized. Lastly, sorption capacity of miscanthus and willow was tested at higher lead contaminant concentrations (up to 300 mg per litre) in order to characterize the sorption isotherm of the materials.

## Materials

*Feedstock collection and processing*

Shrub willow (*Salix viminalis* × *Salix miyabeana*, cv. “Fabius”) stems were harvested by hand during the winter dormant season from the Penn State Research Farm, Rockview site in central Pennsylvania (USA). The willow stems were then chipped using a drum chipper and allowed to dry indoors (20 °C, 50% relative humidity (RH)). The dried chips were then ground in a rotating knife mill (Munson SCC-10-S; Munson Machinery, Utica NY, USA) using either a 3 mm, 6 mm, or 12 mm screen to create three size distributions. Similarly, stems of *M. giganteus* were grown at the university research farm’s Rock Springs site (Rock Spring, PA, USA), and were harvested by hand in late fall after senescence and drying of the plant tissue. The stems were not chipped but were directly ground using the knife mill to create ground material of three particle size distributions. Torrefaction was performed *via* placing approximately 50 g of raw, ground biomass in a thin layer on a tray in a muffle furnace (Lindberg Blue BF51828C-1; Thermo Fischer Scientific, Watham, MA, USA) equipped with a nitrogen purge system running at a rate of 3 L/min. The samples were then heated at a rate of up to 25°/min until the setpoint was reached, at which point the temperature was held steady for 60 min. The samples were then removed from the oven and allowed to sit exposed to open air for 24 h prior to being placed in storage containers.

The alkaline treatment was performed by submerging 45 g of ground feedstock in 100 mL of 0.01 g/mLNaOH solution and placing it in an autoclave at 121 °C/15 psi for 60 min. The samples were then filtered through a cloth filter and washed with deionized (DI) water until a neutral pH was obtained, after which they were oven-dried at 95 °C for 24 hours before being placed in storage containers.

## Methods

*Sorption capacity measurement*

Prior to the experiment, a subsample of approximately 2 g was used to measure the moisture content (wet basis) of the biomass for each treatment, after being dried in a lab oven at 95 °C for 24 h. This allowed the subsequent calculations to be completed on a dry mass basis. A total of 5 g of the undried sample were then added to a beaker with 100 mL of contaminated water. The sample was left in contact with the contaminated water for 20 min, and was manually stirred for 30 s every 5 min. After this, the liquid was filtered from the sample using filter paper in a funnel, and the filtrate was then collected in a capped vial for testing. Samples of the treated water, along with blanks (samples in which no biomass was mixed with the contaminated water), were then tested for their lead concentration using an atomic absorption spectrometer (Perkin Elmer AAnalyst 800, Waltham, MA, USA). The samples were diluted to bring the lead concentration within the equipment’s calibration range before being acidified with nitric acid to achieve a pH of 2.5.

The following performance measures were then calculated for each sample,

$$\eta = (V * (C_A - C_B)) / M_B \tag{3}$$

$$\%_R = 100 * (C_A - C_B) / C_A \tag{4}$$

where $\eta$ is the lead sorption capacity (mg lead per g biomass), $\%_R$ is the amount of lead removed from solution (%), $V$ is the volume of contaminated water used in the test (L), $C_A$ is the lead concentration at start of the test (mg L$^{-1}$), $C_B$ is the lead concentration at end of the test (mg L$^{-1}$), and $M_B$ is the mass of biomass used in the test (unit).

The values of $C_A$ were adjusted downward to account for sorption by the filter paper used in the experiment, by using the “filter blank” value (the concentration measured after the solution was passed through a clean, unused filter paper).

### *Data analysis*

Data visualization was employed to identify apparent trends in the results, and the impact of each variable on performance was assessed using several statistical tests (Microsoft Excel v2016, Microsoft Corporation, Redmond, WA, USA; Minitab v18, Minitab Corporation, State College, PA, USA). A paired t-test was used to test for differences in performance for the two feedstocks, as well as the impact of alkaline treatment on sorption performance. A regression analysis was utilized to characterize the impact of contaminant concentration and particle size on sorption performance. Tukey’s HSD (Honest Significant Difference) test was utilized to test for the impact of torrefaction temperature on the samples of willow and miscanthus. All statistical tests were performed at a confidence level of $\alpha = 0.05$, or 95% confidence. Finally, a least squares approach was used to evaluate the degree to which the sorption data followed the Langmuir isotherm.

## RESULTS AND DISCUSSION

The lead sorption capacity for all treatments varied from 0.15 mg Pb/g to 0.26 mg Pb/g of biomass, with an overall mean of 0.22 mg Pb/g. The percent removed varied from 54.3% to 93.6%. Comparison of the data for the two species *via* paired t-tests did not detect a statistical difference between the two types of biomass in terms of sorption capacity or percent of Pb removal (Table 2).

**Table 2.** Comparison of Sorption Performance: Willow *vs.* Miscanthus

| | Willow | Miscanthus | P Value |
|---|---|---|---|
| Sorption Capacity | 0.2157 (0.0287) | 0.2199 (0.0264) | 0.151 |
| % Removed | 76.85 (10.47) | 76.12 (8.74) | 0.391 |

The values in parenthesis are standard deviations.

In terms of the percent of Pb removal, these results were consistent with the performance of biomass materials used in other studies, but the sorption capacity was much lower than what was reported in other studies. However, the lead contaminant concentration tends to be much higher in most studies, often 10 g/L, whereas this study used a contaminant concentration of 0.015 g/L (Martin-Lara *et al.* 2010). While the higher concentrations used in other studies may be useful for demonstrating absolute maximum sorbance capacities, the concentrations used in this study were more reflective of lead contaminant concentrations that are likely to be encountered in the field (Adelekan and Abegunde 1992; Lee *et al*. 2005; Buragohain *et al*. 2010), although they were still higher than the allowable levels for drinking water (Carney 1991).

## Impact of Particle Size

The sorption capacity of miscanthus did not exhibit variation with particle size ($p = 0.81$), whereas the sorption capacity of willow did vary with particle size ($p = 0.00001$). Furthermore, a regression of sorption capacity *vs*. particle size indicated that the willow sorption capacity decreased 0.009 mg sorbed per gram of sorbent for every mm increase in nominal particle size (Fig. 1).

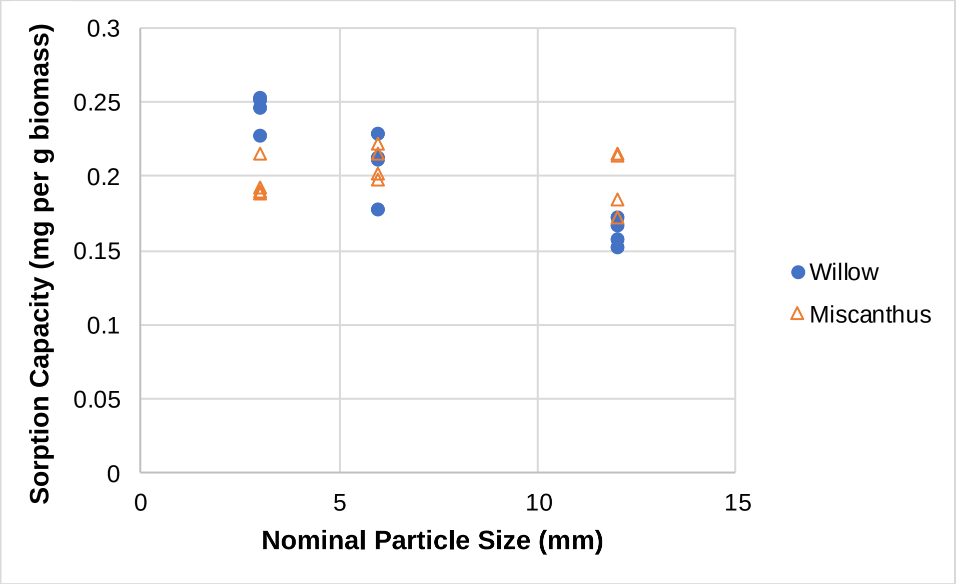

**Fig. 1.** Sorption capacity *vs.* particle size

This difference in performance between the two species could have been due to a more “open” structure of the miscanthus biomass, which allows access to sorption sites within the particles even when the size has not been reduced. Anecdotally, the wetted miscanthus samples were observed to fill a larger portion of the test vessels than the willow, and the measured bulk density of the ground willow was greater than that of the miscanthus (216 vs 78 kg $m^{-3}$). The implication of this result was that in the case of lead sorption, Miscanthus may hold a processing cost advantage over willow, as the desired sorption capacity could be achieved with a lower amount of commutation (and associated cost). However, the sorption capacity of willow may exceed that of miscanthus if the nominal particle size is 3 mm or smaller.

## Impact of Lead Concentration

The sorption capacity for the samples tested varied considerably (coefficient of variation = 0.786) and exhibited an apparent linear increase with increasing contaminant concentration (Fig. 2).

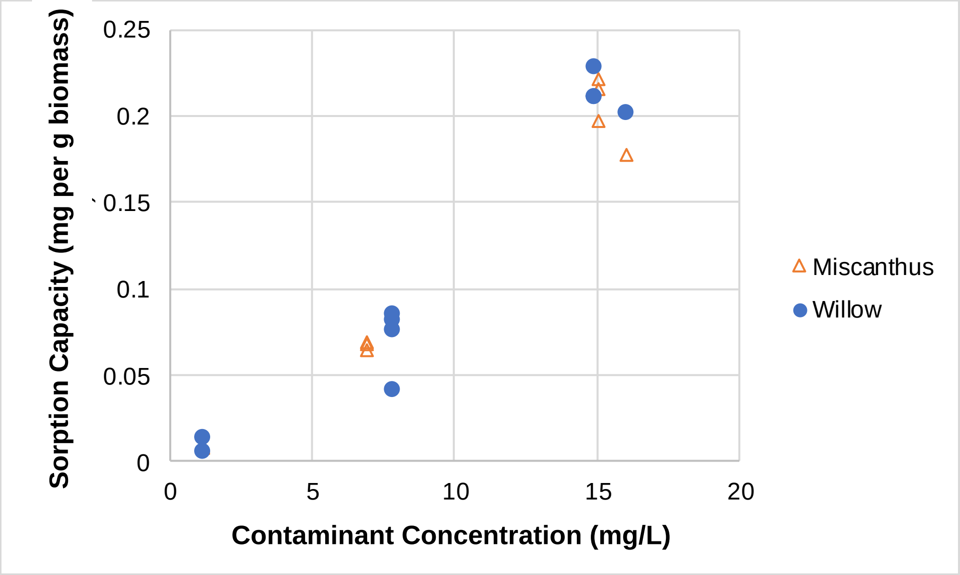

**Fig. 2.** Sorption capacity *vs.* contaminant concentration

The linear regression model yielded a p-value of 0.77 for feedstock type, which indicated that sorption capacity can be considered independent of feedstock type but yielded a p-value < 0.0001 for concentration. The linear regression equation for sorption capacity as a function of contaminant concentration was:

$$\eta = -0.012744 + 0.01574 * C_A \tag{5}$$

The percent of Pb removal was less variable with respect to contaminant concentration (Fig. 3), with a coefficient of variation of 0.230 for all data.

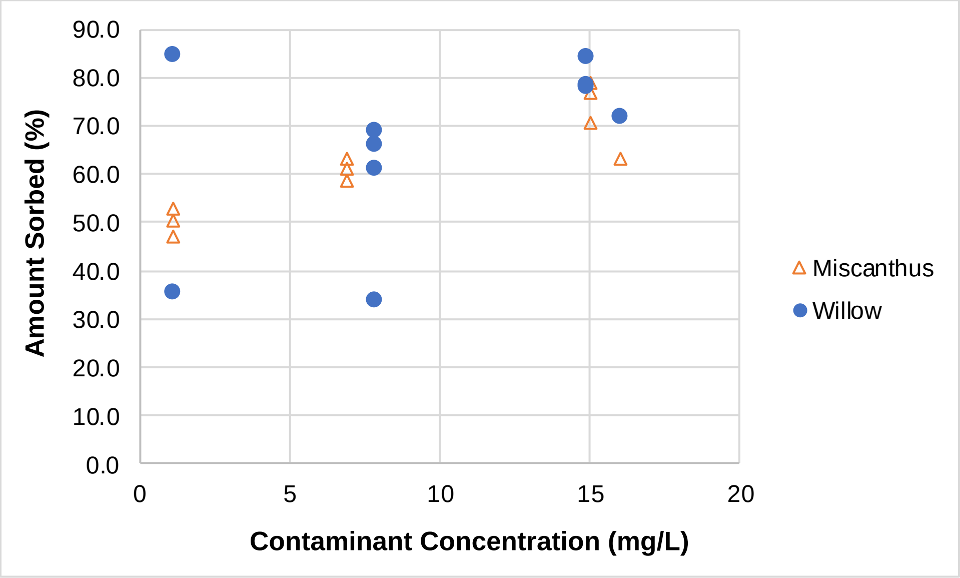

**Fig. 3.** Sorption removal *vs.* contaminant concentration

The linear regression for the percent removal *vs.* concentration gave an adjusted $R^2$ value of 0.3509 (equation not shown), as opposed to 0.9639, which was obtained by Eq. 5.

This was similar to the findings of Anwar *et al.* (2010), although the sorbent material was different (banana peel) and the contaminant concentrations were much higher than those found in this study. These results suggest that the percentage of removal may be a more robust descriptor of sorbent performance, especially in systems where the contaminant concentration can vary.

## Effect of Torrefaction

While torrefied biomass is often reported to have hydrophobic properties, little to no difficulty was encountered in mixing the torrefied samples with the contaminated water. The sorption capacity of raw and torrefied samples is shown in Fig. 4, with results of Tukey's HSD test in Table 3.

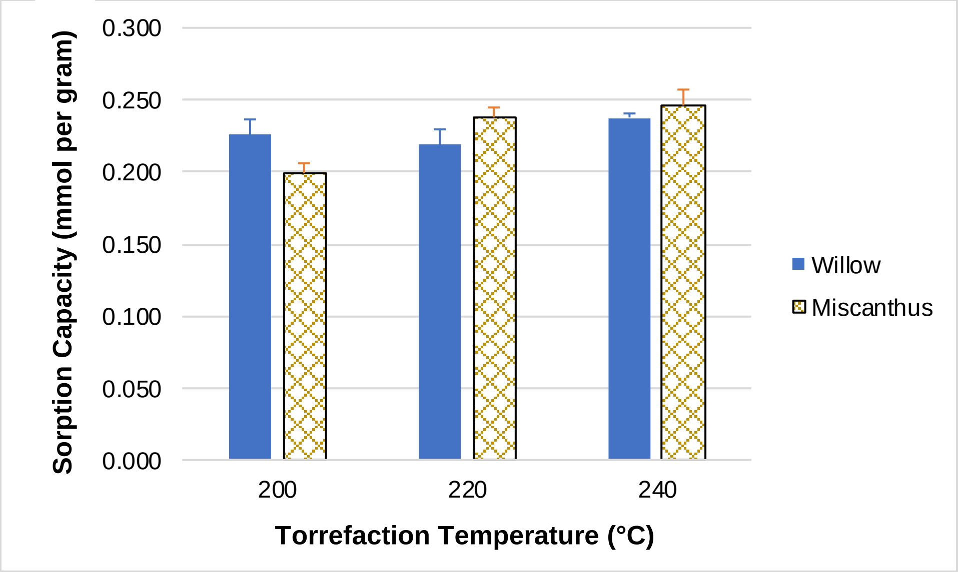

**Fig. 4.** Sorption capacity *vs.* torrefaction temperature

**Table 3.** Sorption Capacity of Raw and Torrefied Samples

| Feedstock and Torrefaction Temperature | Mean | Std Dev | Grouping |
|---|---|---|---|
| Willow, Raw | 0.2174 | 0.0097 | B C D |
| Willow, 200 | 0.2260 | 0.0104 | A B C |
| Willow, 220 | 0.2190 | 0.0109 | B C D |
| Willow, 240 | 0.2373 | 0.0031 | A B C |
| Miscanthus, Raw | 0.2120 | 0.0125 | C D |
| Miscanthus, 200 | 0.1987 | 0.0081 | D |
| Miscanthus, 220 | 0.2375 | 0.0077 | A B |
| Miscanthus, 240 | 0.2373 | 0.0031 | A |

The willow did not show any differences in sorption capacity between treatments, but miscanthus torrefied at higher temperatures (220 °C, 240 °C) was statistically different than the raw miscanthus that was torrefied at a lower temperature (200 °C). This result suggested that, while torrefaction did not impact the sorption capacity for willow, higher temperature torrefaction treatment did impact the sorption capacity of miscanthus, increasing its capacity to adsorb lead. The reason for this difference in performance between the two feedstocks was not readily apparent. The observed differences in performance may be related to microstructural differences in the lignocellulosic arrangement of the two feedstocks, such that torrefaction increased the number of available sites for sorption in miscanthus but did not have a similar impact on willow. Also, it is conceivable that volatilized torrefaction products were reabsorbed differently on the two feedstocks, given differences in lignin composition between herbaceous and woody materials.

## Impact of Alkaline Treatment

A paired t-test comparison of means indicated that the alkaline treatment did not have an impact on the sorption capacity for willow but did influence the capacity for miscanthus ($p < 0.05$, Fig. 5).

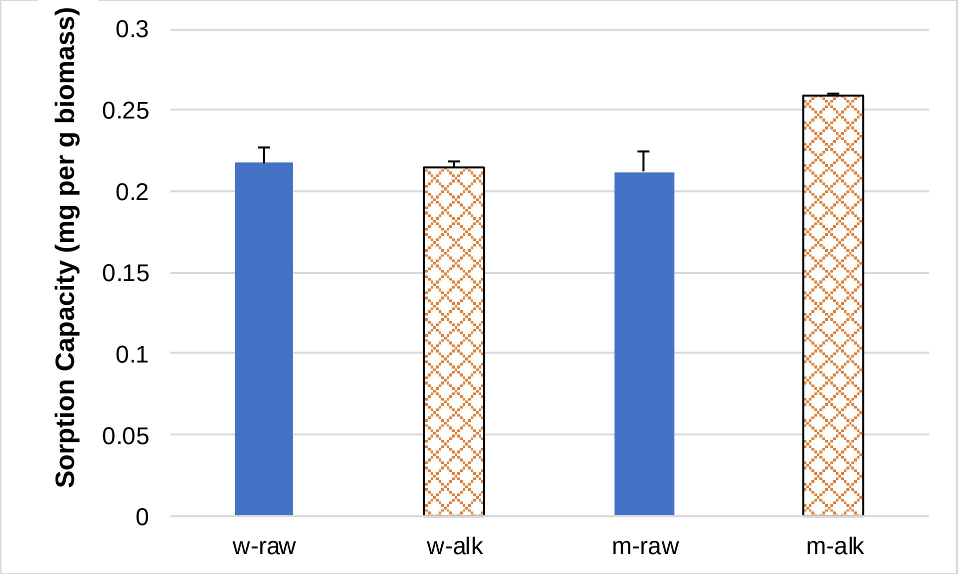

**Fig. 5.** Sorption capacity for raw and alkaline treated samples (w = willow, m = Miscanthus)

The willow was not impacted by alkaline treatment, whereas miscanthus' sorption performance was enhanced. This was similar to the effect of torrefaction. Again, the cause of this difference was not readily apparent, but it may have been related to microstructural or chemical differences between the woody willow and the herbaceous miscanthus. Willow, which was observed to occupy less volume than miscanthus when placed in water, may have a smaller effective surface area on which an alkaline solution can act, thus reducing the alkaline treatment's effectiveness. Also, lignin in miscanthus contains guaiacyl, syringyl, and p-hydroxyphenyl monomeric units, while lignin from willow biomass generally does not contain p-hydroxyphenyl monomeric units (Campbell and Sederoff 1996; El Hage *et al.* 2009) – this difference in lignin could lead to different responses to akaline treatment. These varying responses to treatments (commutation, torrefaction, alkaline treatment) indicate that, ultimately, a robust understanding of adsorption by dedicated biomass crops needs to take into account the multiple constituent components of the biomass, its physical structure, and the effect of various treatments on their performance.

## Comparison of Isotherms

The sorption isotherms for miscanthus and willow are shown in Fig. 6, with a least squares fit line for both the Langmuir and the Freundlich Isotherm.

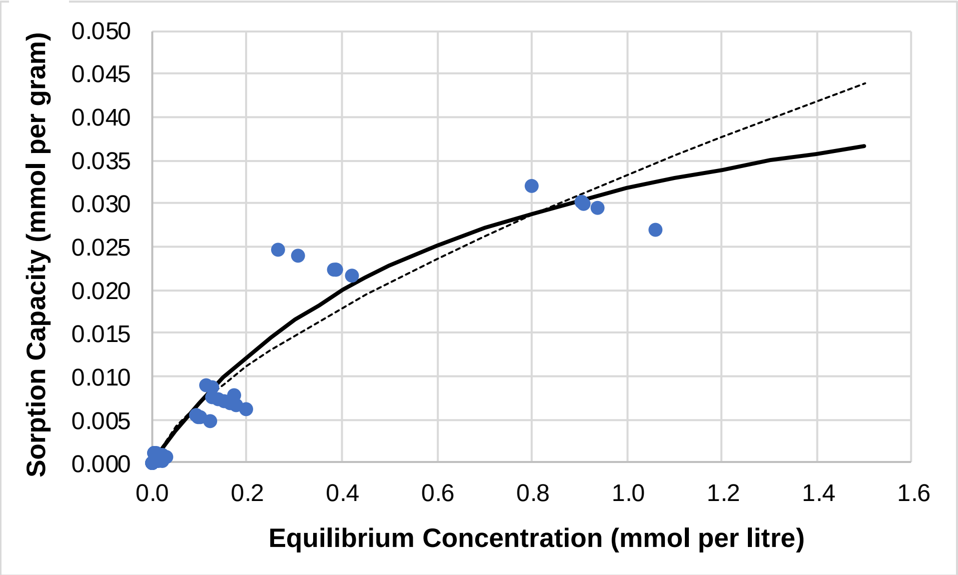

**Fig. 6.** Langmuir (solid line) and Freundlich (dashed line) isotherms for measured data

The Langmuir isotherm fit the measured data more closely than Freundlich, with a Mean Absolute Error (MAE) of 0.0014 mmol $g^{-1}$ and a Mean Relative Absolute Error (MRAE) of 0.90, compared to 0.0018 and 2.98 for the Freundlich Isotherm. Coefficients for the two isotherms were: Langmuir $q_m = 0.0525$ and $b = 1.530$, Freundlich $K_f = 0.0333$ and $n = 1.472$. Nonlinearity in the isotherm is apparent only at relatively high equilibrium concentrations, which suggests that modeling sorption capacity as a linear function of $C_e$ may be sufficient for most practical applications, since lead concentrations in contaminated water tend to be at the lower range of values tested here. The variability of performance relative to the isotherm, evidenced by MRAE values of 0.90 and 2.98 for the two isotherms, may be related to variability inherent to biological materials and/or the relatively small sample sizes used. Questions related to full system performance, sorbent regeneration, and scaleup remain an opportunity for ongoing research in this area.

## CONCLUSIONS

1. Both willow and miscanthus were effective as a sorbent for lead in contaminated water. Sorption capacities ranged from 0.15 mg to 0.26 mg lead per gram of biomass when tested at contaminant concentrations ranging from 1 mg to 15 mg lead per litre. The percent removal ranged from 54.3% to 93.6%, which was similar to values reported for other forms of biomass.
2. Willow and miscanthus did not exhibit a systematic difference in sorption performance, although some pretreatments did affect the two feedstocks differently. Grinding the feedstock to a different particle size impacted the willow's sorption capacity, but not

that of miscanthus. Torrefaction or alkaline treatment did not impact the willow's sorption capacity, but they did impact that of miscanthus.

3. Sorption capacity of willow and miscanthus both fell on the same isotherm, and also followed the same trend with respect to contaminant concentration.
4. These results suggested that either of these feedstocks was an effective sorbent for treatment of lead contaminated water, and that miscanthus' performance was enhanced by torrefaction as well as alkaline treatment.

## ACKNOWLEDGMENTS

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