

FEASIBILITY OF REMOVING FURFURALS FROM SUGAR SOLUTIONS USING ACTIVATED BIOCHARS MADE FROM AGRICULTURAL RESIDUES

K. Thomas Klasson,* Minori Uchimiya, Isabel M. Lima, and Larry L. Boihem, Jr.

Lignocellulosic feedstocks are often prepared for ethanol fermentation by treatment with a dilute mineral acid catalyst that hydrolyzes the hemicellulose and possibly cellulose into soluble carbohydrates. The acid-catalyzed reaction scheme is sequential, whereby the released monosaccharides are further degraded to furans and other chemicals that are inhibitory to the subsequent fermentation step. This work tests the use of agricultural residues (e.g., plant waste) as starting materials for making activated biochars to adsorb these degradation products. Results show that both furfural and hydroxymethylfurfural (HMF) are adsorbed by phosphoric acid-activated and steam-activated biochars prepared from residues collected from cotton and linen production. Best results were obtained with steam-activated biochars. The activated biochars adsorbed about 14% (by weight) of the furfurals at an equilibrium concentration of 0.5 g/L, and by adding 2.5% of char to a sugar solution, with either furfural or HMF (at 1 g/L), 99% of the furans were removed.

Keywords: Sugar; acid hydrolysis; inhibitors; activated biochar; furfural; biofuels; furans

Contact information: USDA, ARS, Southern Regional Research Center, 1100 Robert E. Lee Blvd., New Orleans, LA 70124, USA; *Corresponding author: thomas.klasson@ars.usda.gov

INTRODUCTION

It has been argued for many years that agricultural byproducts represent a potentially valuable resource for production of biofuels, chemicals, and bioproducts. In a recent report, it was estimated that 129 and 176 million dry metric tons are currently available from forestry and agriculture industries in the U.S. for producing bioenergy and bioproducts (Perlack et al. 2005). Fermentation of biomass into ethanol or other products first requires hydrolyzing the carbohydrates into fermentable sugars. Hydrolysis is usually carried out as a two step operation, where the biomass is pretreated in the presence of a dilute mineral acid catalyst, that partially hydrolyzes the hemicellulose, and the cellulose and hemicellulose are subsequently saccharified to monosaccharides using cellulases and other related enzymes. However during pretreatment, sugar and lignin degradation products are produced that are inhibitory (Boyer et al. 1992) to many ethanol-producing organisms and, if not removed, will cause either a stalled fermentation or a prolonged lag phase and reduced product yield. Recently, Mussato and Roberto (2004) reviewed options for detoxifying these hydrolyzates. Many methods that have been studied in the past focused on pH adjustment in combination with activated charcoal treatment but, in most of the cases, the focus was detoxification for the purpose of

fermentation (Gong et al. 1993; Dominguez et al. 1996; Parajo et al. 1996; Alves et al. 1998; Silva et al. 1998; Mussatto and Roberto 2001), rather than characterizing the chemicals adsorbed onto the chars.

Methods for collecting furfural are also of broader interest because furfural has been detected as an environmental contaminant from oil refineries and, in fact, activated carbon has been suggested as an adsorption treatment method (Sulaymon and Ahmed 2008). In this article we report on adsorption of furfural and hydroxymethylfurfural, two common acid-hydrolysis compounds that are inhibitory to fermentation, onto un-activated and activated biochars made from normally discarded agricultural resources.

EXPERIMENTAL

Materials

Cotton seed hulls, dew-retted flax stem shive, and cotton gin waste were obtained, sized, pyrolyzed, and activated. In total, nine experimental chars were evaluated: cotton seed hull chars (CH Char) pyrolyzed at five different temperatures, two steam activated (SA) chars (from flax shive and cotton gin waste), and two phosphoric acid-activated (PA) chars (from flax shive and cotton gin waste). Briefly, the different preparations were as follows:

- (i) Cotton seed hull (as received) chars were prepared by pyrolysis at 200, 350, 500, 650, and 800°C for 4 h under nitrogen atmosphere (Uchimiya et al. 2011);
- (ii) Ground (0.84 to 2 mm) flax shive and cotton gin waste were pyrolyzed at 700°C for 1 h under nitrogen and activated with steam at 850°C for 1.5 h (Klasson et al. 2009a); and
- (iii) Ground flax shive and cotton gin waste were soaked in 30% phosphoric acid (1:1 w:w ratio) over night, activated at 450°C for 4 h in an air atmosphere, and thoroughly washed (Marshall et al. 2007; Klasson et al. 2009a).

For comparison purposes, a commercially available steam activated carbon (bituminous-based, Filtrasorb 400, Calgon Carbon, Bay St. Louis, MO) was included in the study. Furfural (2-furfuraldehyde), 5-hydroxymethylfurfural (HMF), glucose (dextrose), D-xylose, and high-pressure liquid chromatography (HPLC) solvents were of analytical grade and were obtained from various vendors.

Methods

Two types of adsorption studies were conducted and, in all cases, experiments were done in triplicates. In the first screening study, the furfurals were dissolved (separately) in deionized water at a concentration of 1 g/L. Ten milliliters of this solution were mixed (end-over-end) in 40-mL glass vials (National Scientific, Rockwood, TN) with 0.1 g of char/activated char for 24 h. After contact, a portion of the supernatant was filtered using 0.45- μ m-pore-size syringe filters (Millex-FH, polytetrafluoroethylene, Millipore, Billerica, MA) before analysis.

For the isotherm study, solutions consisting of 1 g/L of furfural (or HMF), 20 g/L D-xylose, 30 g/L glucose, and a few crystals of thymol (to prevent microbial growth)

were prepared in deionized water or in an acetate buffer (88 mL 0.2 M acetic acid plus 12 mL 0.2 M sodium acetate per L, pH=5.6–6.0). Ten milliliters of either of these solutions were mixed with various quantities of char (0, 0.01, 0.03, 0.05, 0.08, 0.14, and 0.25 g) as described above for the screening study; likewise, liquids were filtered before analysis. All the studies were performed at ambient temperatures.

Furfural and HMF analyses were performed via HPLC (Series 1100, Hewlett Packard/Agilent, Santa Clara, CA) by combining 300 μ L of filtered sample with 700 μ L of ethyl acetate in a 2-mL HPLC automatic sampler vial, mixing the vial for 10 s using a vortex mixer, and injecting 10 μ L of the top organic phase into isopropanol/acetonitrile (30/70, vol%/vol%) mobile phase that was passed through a Nova-Pak C18 column (3.9 \times 300 mm, 4 μ m particle size, Waters Corp., Milford, MA) using a flow rate of 0.8 mL/min at 22°C. The diode array detector collected data at a wavelength of 280 nm. Calibration was performed with four furfural standards (0, 0.3, 0.7, and 1.0 g/L) prepared using the same technique as for samples. The calibration curve was found to be linear with similar slopes for both furfural and HMF. Neither sugars nor acetic acid buffer appeared to affect furfural (or HMF) extraction efficiency or furfural (or HMF) analysis, within the analytical reproducibility. Solutions containing activated char and sugars were also used as controls to investigate if any compounds were desorbed from the material that would interfere with the HPLC analysis method. No such compounds could be detected.

RESULTS AND DISCUSSION

Cotton hull chars did not adsorb appreciable amounts furfural [see Figure 1 (a)]. In contrast, steam activated chars prepared from cotton gin trash and flax shive adsorbed at least as much furfural as a commercially available carbon product. Phosphoric acid activated chars prepared from cotton gin trash and flax shive each adsorbed similar amounts of furfural but only half as much as their steam activated counterparts.

Similarly, only the activated chars and the commercial activated carbon adsorbed appreciable amounts of HMF [see Figure 1(b)]. As in the case with furfural, phosphoric acid activated chars prepared from cotton gin trash and flax shive adsorbed similar amounts of HMF but only half as much as their steam activated counterparts.

Unactivated chars created at low temperatures do not have significant surface areas (Shenxue 2004; Lehmann 2007), such as in the case with cotton seed hulls, which had no measurable surface area when the pyrolysis temperature was 650°C, or below. At 800°C pyrolysis temperature, the surface area was 322 m²/g but was lacking many active surface groups (Uchimiya et al. 2011). Phosphoric acid and steam activation of chars produces significant surface area, as was the case here, where the surface area for phosphoric acid activated materials (from cotton gin waste and flax shive) was between 582 and 674 m²/g and 726 to 923 m²/g, in the case of steam activation (Klasson et al. 2009a). However, previous studies have shown that the chemical properties of the surfaces are highly dependent on activation strategy. Phosphoric acid activation generates areas that are highly polar, depending on the oxidative conditions during pyrolysis, while not changing the total area (Klasson et al. 2009b). It is possible that the

lower surface area, lack of appropriate chemically active surface groups, or the polarity contributed to the lower adsorption onto these materials [see Figure 1(a) and (b)].

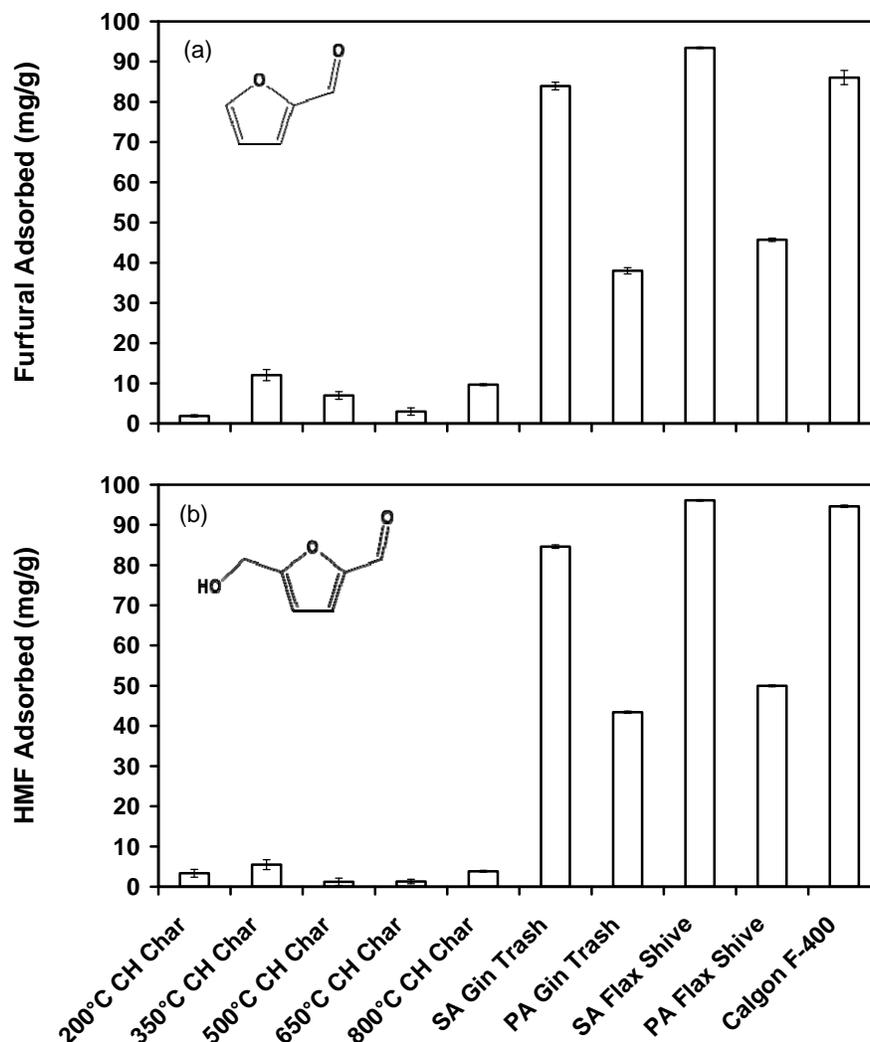


Fig. 1. Adsorption of furfural (a) and HMF (b) from water by cotton seed hull (CH) chars and steam (SA) or phosphoric acid (PA) activated gin trash or flax shive chars. A commercial product (Calgon F-400) is included for comparison. Error bars correspond to standard deviation values from results of triplicate experiments.

The adsorption of organics on carbon is due to physical adsorption by London forces. Manes (1998) suggests that this type of adsorption can be described by the Polanyi potential theory, which assumes that an adsorption space exist in the pores of the chars, where the potential energy of the solute is lower than in the bulk phase. While initially developed for gas phase adsorption, the theory has been modified to handle almost any kind of adsorption system (Manes 1998), such adsorption of solutes from liquids in our case. The importance of this theory is that no emphasis is placed directly on surface area but on energetic regions within the pores where adsorption take place.

This means that surface area is necessary but not sufficient to predict adsorption, which is why feasibility studies such as those presented here are beneficial.

Based on the screening studies, steam-activated char prepared from flax shive was selected for isotherm studies. The studies were performed in both buffered and un-buffered sugar solutions. The results are shown in Fig. 2. As is noted, only minor differences were observed for furfural adsorbed in buffered versus un-buffered solutions, where adsorption was slightly better in the buffered solution [see Fig. 2(a)].

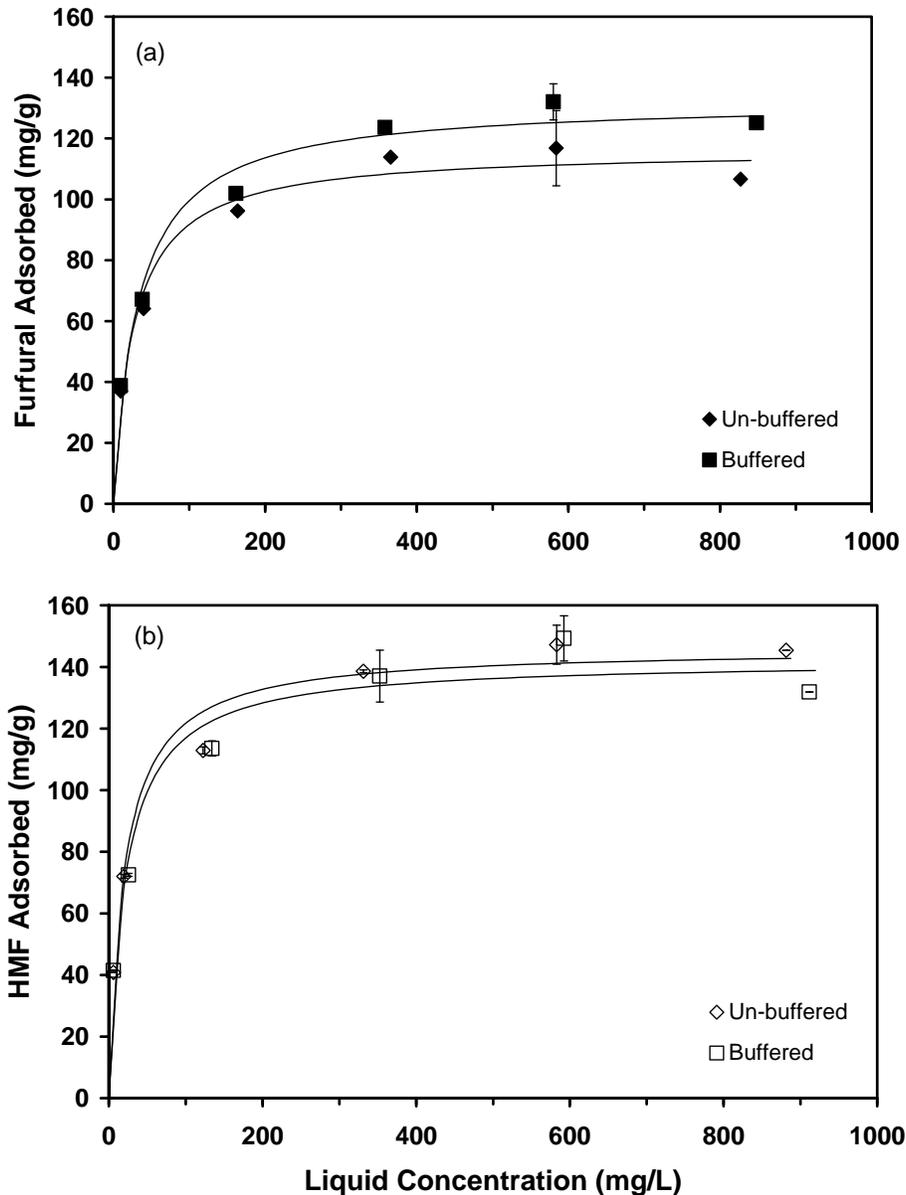


Fig. 2. Results of isotherm study using either furfural or HMF in buffered or un-buffered sugar solutions in contact with steam-activated flax shive chars. Curves represent best fit using the Langmuir isotherm correlation.

HMF adsorption appeared to be the same in buffered and un-buffered solutions [see Fig. 2(b)]. Also shown in Fig. 2 are the best fit Langmuir isotherm curves as determined by classic least square non-linear regression (Duggleby 1981). The parameters for the Langmuir equation are shown in Table 1, together with confidence interval (using the t-distribution at a 95% confidence interval) for each parameter. It is important to note that the shape of the isotherm was steep at low liquid concentrations, which is beneficial as the maximum capacity of the sorbent was reached even at relatively low concentration of furfurals in the liquid. The pH in the solution post-contact was pH 3.1 to 7.3 (lower pH for HMF than for furfural and lower pH with increasing char amounts) in the case of un-buffered solutions and pH 5.5 to 6.2 in the case of the buffered solutions. The pH used in our experiments should have little effect on the dissociation of protons from the furans, as the pK_a -value is assumed greater than 12 for both of them (Weng et al. 2010; Qi et al. 2011). Without dissociation, the adsorption should not be significantly impacted by pH (Manes 1998).

Table 1. Determined Values of Langmuir Isotherm Parameters, where q is Amount Adsorbed and $[c]$ is the Liquid Phase Concentration at Equilibrium.

		Parameter values for $q = q_m k [c] / (1 + k [c])$		Correlation coefficient
		q_m	k	R^2
Furfural	Un-buffered	116±6	0.0373±0.0110	0.94
	Buffered	132±6	0.0305±0.0077	0.96
HMF	Un-buffered	146±6	0.0500±0.0110	0.97
	Buffered	142±8	0.0465±0.0147	0.94

Most previously reported results have focused, not on individual inhibitors but, on removal of phenolics by activated charcoal and what benefit this had for fermentation. Mussatto and Roberto (2001) reported improved fermentation yields when 2.5% (w/w) activated charcoal removed 27% of the phenolics in hydrolyzate. Silva et al. (1998) reported that 1% (w/w) active charcoal removed 94% of phenolics, when used in combination with aluminum salts. Alves et al. (1998) reported that, in experiments with factorial design, 2.4% activated charcoal added to sugarcane bagasse hydrolyzate resulted in an optimal fermentation product yield. Gong et al. (1993) and Dominguez et al. (1996) used activated charcoal or a strong acid cation-exchange resin to remove (what was only characterized as) fermentation inhibitors. In one case, better fermentation results were obtained with charcoal-treated hydrolyzates; in another case, the resin gave the better results. The studies above use adsorbents characterized as active charcoal or activated charcoal, but most published reports have provided inadequate information about the activation process. In one study, Parajo et al. (1996) reported that charcoal was activated by equilibrating charcoal with 0.4 M hydrochloric acid. This method is quite different from the steam or acid activation processes that were used to generate the chars in this study (Klasson et al. 2009a). It should be noted that the chars made from cottonseed hulls, cotton gin waste, and flax shive used in studies herein were washed with 0.1 M hydrochloric acid and rinsed in water (Klasson et al. 2009b; Uchimiya et al. 2011).

Sahu et al. (2008a) reported on adsorption of furfural from water (without sugars) onto a coconut shell-based steam-activated carbon. Best adsorption was seen at approximately pH 6, or above, and their isotherms showed that a maximum of 23 mg furfural was adsorbed onto 1 g of activated carbon at ambient temperature. This is about 5 times less than what was observed in our studies [see Fig. 2(a)]. The same research group studied how well bagasse fly ash could adsorb furfural (Sahu et al. 2008b). In these studies, the fly ash adsorbed a maximum of 82 mg/g of furfural, about 40% less than what is herein reported in Fig. 2(a). The k -values listed in Table 1 for furfural are similar to those obtained by Sahu et al. (2008a; 2008b), indicating the beneficial steepness in the isotherm. The maximum adsorption capacities (q_m), reported in Table 1, are slightly lower than those reported by Weil et al. (2002), who studied furfural adsorption on two polymeric adsorbents. In those studies, the adsorbents were able to retain 176 to 185 mg/g of furfural at 30°C. Furfural removal from water by coconut shell based activated carbon was investigated by Sulaymon and Ahmed (2008). In these studies, the Langmuir isotherm was used to describe the adsorption isotherm, and the q_m value was determined to be 374 mg/g, which is three times higher than the values reported herein and 15 times higher than those reported by Sahu et al. (2008a) on a similar activated carbon. Neither of the studies reported above focused on HMF.

Acetic acid can also be classified as a fermentation inhibitor. Berson et al. (2005) showed that, in synthetic hydrolyzate, approximately 14 mg/g of acetic acid was adsorbed on activated carbon at an equilibrium concentration of 0.5 g/L and, at 1 g/L, the capacity increased to 24 mg/g. While acetic acid adsorption was not investigated in our studies, it is interesting to note that the acetate/acetic acid (~1.5 g/L) in our buffered solution did not appear to interfere with the adsorption of furans (Fig. 2).

The dosing requirement; e.g., how much activated char would be needed to reduce furfural from an inhibitory level to a non-inhibitory level, can easily be calculated from the isotherm equations presented in Table 1. The relationship is linear, as seen in Fig. 3, where the dosing requirement has been plotted as a function of the initial furfural concentration for several desired (non-inhibitory) levels. The inhibitory levels vary from organism to organism but are general below 1 g/L (Weil et al. 2002; Mussatto and Roberto 2004), and furfural is more toxic than HMF.

CONCLUSIONS

1. The feasibility of removing two common fermentation inhibitors, furfural and hydroxymethylfurfural, using pyrolytic products made from agricultural byproducts has been demonstrated.
2. Steam-activated chars made from cotton gin waste or flax shive appeared to work well for both furfural and hydroxymethylfurfural, and only moderate amounts would be needed to reduce these compounds to low concentration in process streams.
3. The results showed that un-activated chars made from cotton seed hulls were not effective in removing furfural or hydroxymethylfurfural.

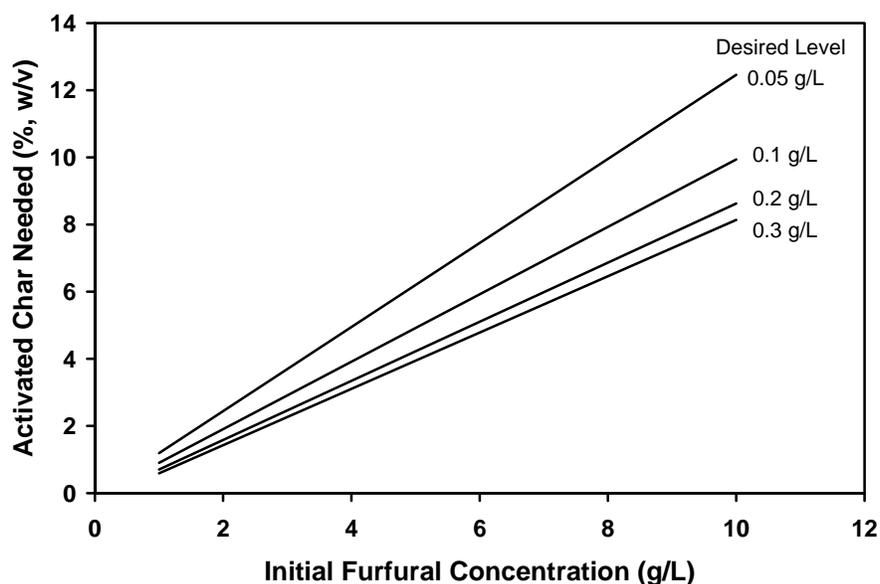


Fig. 3. Estimated steam activated char dosing requirement to remove furfural to a desired level ($q_m=132$, $k=0.0305$).

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