SEPARATIONS

Removal of Fermentation Inhibitors Formed during Pretreatment of Biomass by Polymeric Adsorbents

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The production of aldehydes that are microbial inhibitors may occur when hexoses and pentoses in an aqueous solution are exposed to temperatures above 150 °C under acidic conditions common to acid-catalyzed lignocellulose biomass pretreatment. Concentrations greater than 0.1% of the degradation product, furfural, strongly inhibit fermentation, as was confirmed for hydrolysate that contained 0.5% (w/o) furfural. Methods of furfural removal that have been reported include sulfite or alkali addition to achieve chemical reduction, ion exchange, hydrophobic adsorption, and irreversible adsorption on activated carbon. This paper reports the removal of furfural from biomass hydrolysate by a polymeric adsorbent, XAD-4, and desorption of the furfural to regenerate the adsorbent using ethanol. Liquid chromatographic analysis showed that furfural concentrations were less than 0.01 g/L compared to the initial concentrations that were in the range of 1–5 g/L. Fermentation of the resulting biomass hydrolysate with recombinant Escherichia coli ethanologenic strain K011 confirmed that the concentration of furfural in the hydrolysate caused negligible inhibition. Fermentation of XAD-4-treated hydrolysate with E. coli K011 was nearly as rapid as the control medium that was formulated with reagent-grade sugars of the same concentration. Ethanol yields for both fermentations were 90% of theoretical. Modeling of the adsorptive properties of this styrene-based adsorbent indicates that it is suitable for on–off chromatography and could be useful in a continuous processing system for removing small amounts of aldehydes that might otherwise inhibit fermentation.

Introduction

Fuel ethanol production in the U.S. is more than 1.8 billion gal/yr. Any process developments that can increase the production of ethanol are beneficial. One possibility of increasing ethanol production is by increasing the amount of carbohydrates fermented from corn. Corn fiber, a waste product used for animal feed, is a good candidate for additional sugar production to enhance ethanol yield. Dry corn fiber is composed of approximately 30% glucan from starch and cellulose and 25% xylan from hemicellulose. Corn fiber is readily available for fermentation because it is produced at wet-milling plants.

Three general steps are needed to convert the polysaccharides, cellulose, and hemicellulose in corn fiber to sugars usable for fermentation. First, the fiber is pretreated to modify the chemically resistive crystalline polysaccharides to a more reactive amorphous form. Second, the pretreated fiber is converted to monosaccharides by enzymatic or acid hydrolysis of the polysaccharides. Third, the sugars are fermented to value-added products such as ethanol. The pretreatment step presents the greatest technical challenge because this is the stage at which microbial inhibitors are formed. A great array of pretreatment technologies exist that use chemical additives and/or heat to improve the reactivity of plant cellulose to hydrolysis.1 Of these technologies, hot-water pretreatments show promise because they produce high yields (> 90%) of xylose and xylan through solubilization of the hemicellulose while minimizing degradation to furfural. Through careful selection and control of pretreatment temperature and pH conditions, the formation of inhibitors can be minimized.2,3

Pretreatment. Water is an effective solvent for the pretreatment of corn fiber. Water is nontoxic and compatible for enzymatic hydrolysis of cellulose and hemicellulose. The optimal conditions for decrystallizing cellulose and minimizing inhibitor formation involve controlling the temperature between 160 and 220 °C and pH between 5 and 7, with higher temperatures required for higher lignin biomass, such as corn residue, than a material that is low in lignin, such as corn fiber.2,4 There are several processes that occur during aqueous pretreatment at high temperatures. Water can act as a hydrating agent, diffusing inside the crystalline regions
of the cellulose and swelling it to disrupt its crystallinity, thus making the cellulose more reactive. Concurrently, when the pH is not controlled, water acts as a weak acid and promotes rapid acid-catalyzed hydrolysis of polysaccharides to monosaccharides, which subsequently degrade to furfural, (hydroxymethyl)furfural (HMF), and other inhibitors. Acid hydrolysis of xylan is particularly problematic because it contains acetyl groups that upon hydrolysis form acetic acid. Xylan is also more readily hydrolyzed to monosaccharides (xylose) than cellulose, which leads to the formation of furfural through xylose degradation (Figure 1). Depending on the microorganism, concentrations as low as 0.1 g/L of furfural can be inhibitory.5,6

Furfural Toxicity. Furfural toxicity has been extensively studied in relation to ethanol production. Escherichia coli strain K011 has a maximum tolerance of 3 g/L.6 However, culture growth and ethanol production begin to be affected at concentrations greater than 1 g/L.6 Other enteric bacteria, including those engineered for ethanol production, have been observed to have similar tolerances (e.g., 3–4 g/L).5–7 Saccharomyces cerevisiae and xylose fermenting yeasts, Candida shehatae and Pichia stipitis, have been observed to be almost completely inhibited by furfural concentrations of 2–4 g/L.8,9 Possible mechanisms for furfural toxicity include chemical reactivity with cellular components, damage to the cellular membrane, and inhibition of metabolism.5,10 The toxicity of furfural appears to be a function of its hydrophobicity. Palmqvist et al. demonstrated a correlation between toxicity and hydrophobicity for a number of inhibitors found in lignocellulose hydrolysates.9,11

The observed toxicity of furfural decreases, somewhat, when a larger inoculum is employed, possibly because many microorganisms are capable of converting furfural to the alcohol form, which is less toxic.6,7,11,12 Selection and screening strategies can also be used to obtain strains that are more tolerant to inhibitors commonly associated with hydrolysates.

Strategy for Avoiding Furfural Inhibition of Fermentation. Furfural inhibition can be avoided by minimizing its formation and/or removing what is formed. Furfural formation can be minimized by carefully controlling the pH, temperature, and residence time during pretreatment.1 Furfural can be removed from the supernatant with the use of polymeric adsor-bents. The criteria for these adsorbents should be a high specificity for adsorbing furfural and little or no specificity for sugars (i.e., glucose or xylose).

A number of methods have been tested for removing furfural and other fermentation inhibitors from lignocellulose hydrolysates. Methods reported in the literature include treatment with alkali, adsorption on activated carbon, adsorption on ion-exchange resins, and adsorption on hydrophobic resins.16 The work presented in this paper evaluates the hydrophobic polymeric adsorbents, XAD-4 and XAD-7, for their ability to adsorb furfural from an aqueous sugar stream as well as the desorption of furfural and regeneration of the resins using alcoholic solvents. The adsorption and desorption properties of these adsorbents were characterized by batch analyses. Based on this characterization, a continuous, XAD-4 packed-bed, on-off adsorption system was built, and the column's dynamic adsorption and desorption capacities were determined. Finally, the effect on fermentability for XAD-4-treated corn fiber hydrolysate was tested.

Materials and Methods

Stationary Phase. The stationary phases for these experiments were the Amberlite polymeric adsorbents XAD-4 and XAD-7 manufactured by Rohm and Haas and purchased from Supelco (Bellefonte, PA). The XAD-4 (lot nos. 62165BAA and 62175GTO) resin is a poly(styrene–divinylbenzene copolymer bead, while the XAD-7 (lot no. 0025002) resin is a methacrylic ester bead. The physical properties of both resins are listed in Table 1. No significant difference in the physical properties or performance between the two lots of XAD-4 resin was measured.

Stationary Phase Preparation. Upon arrival the resins were prepared by washing with 2-propanol at a 4:1 volume ratio of solvent to resin. This step was repeated three times to remove any residual organic compounds present. At the end of the third step, the solvent was separated from the resin by filtering with Whatman No. 42 filter paper. Resin was air-dried for 48 h before use. The air-dried resin was used for the batch studies.

For resin preparation in the adsorption column, the air-dried XAD-4 was reswollen with 2-propanol at a 4:1 volume weight ratio of solvent to resin for 48 h. This slurry was used to pack the column.

Furfural and Glucose and Alcohol Solvents. Furfural from Sigma (St. Louis, MO; 2-furaldehyde, lot no. 16H3532), 6.8 g/mL, was used for the furfural solutions. Glucose (anhydrous D-glucose) was obtained from Mallinckrodt (Paris, KY).

The solvents used to desorb the furfural from the stationary phase were methanol (Fisher Scientific, Pittsburgh, PA), dehydrated, 200 proof ethanol (McCormick Distilling Co. Inc., Brookfield, CT), n-propanol, and n-butanol (Fisher Scientific, Pittsburgh, PA). Media ingredients were supplied by Difco (Detroit, MI).
Table 2. Physical Properties of the XAD-4 Adsorption Column

<table>
<thead>
<tr>
<th>property</th>
<th>value</th>
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</thead>
<tbody>
<tr>
<td>bed height (cm)</td>
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</tr>
<tr>
<td>inside diameter (cm)</td>
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<tr>
<td>bed volume (mL)</td>
<td>156</td>
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<tr>
<td>column void volume (mL)</td>
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</tr>
<tr>
<td>dry weight of XAD-4 inside the column (g)</td>
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<td>solid density, ( \rho_s ) (g/mL)</td>
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<td>external void fraction, ( \epsilon_e )</td>
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<tr>
<td>intraparticular void fraction, ( \epsilon_p )</td>
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<td>pump flow rate (mL/min)</td>
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<td>superficial velocity (cm/min)</td>
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<tr>
<td>interstitial velocity (cm/min)</td>
<td>5.3</td>
</tr>
</tbody>
</table>

**Batch Adsorption.** Various aqueous furfural solutions (0.1, 0.2, 0.4, 0.6, 0.8, and 1.0%) were contacted with XAD-4 [10% (w/v)] for the batch equilibrium studies. Solutions were incubated at 30, 50, and 70 °C for the 4 h with agitation (setting = 8) in a water bath (American Scientific Products, McGaw Park, IL). Each trial was done in triplicate. The solvent was recovered and analyzed for furfural. The difference in furfural concentration in solution between the starting and final solutions was used to calculate the mass of furfural adsorbed by the resin.

**Batch Desorption.** Four different alcohol solvents were evaluated for their ability to desorb furfural from the stationary phase for the batch desorption equilibrium. The alcoholic solvents tested were ethanol, methanol, n-propanol, and n-butanol. XAD-4 and XAD-7 with 0.12 and 0.10 g of furfural adsorbed/g of resin, respectively, were mixed with 15 mL of solvent/g of resin. This mixture was incubated at 50 °C for 90 min with agitation (setting = 8). The solvent was recovered and analyzed for furfural.

**Adsorption Column.** Approximately 160 mL of XAD-4 resin was washed in 2-propanol for 48 h. The swollen resin was then slurry packed into a 72.4 cm 304 stainless steel column with an inner diameter of 1.91 cm. At intervals during the packing, the column was vigorously tapped to prevent bridging of the resin inside the column. The excess resin was removed, and the ends of the column were fitted with flange-plate closures sealed with Teflon O-rings. Liquid was pumped (6 mL/min) through the column using a Milton-Roy minipump. At the completion of the experiments, the column was opened and the bed height (in ethanol) was measured.

**Fermentation Experiment.** E. coli strain K011 was supplied by Dr. L. O. Ingram. E. coli K011 was grown on amended Luria–Bruttani (LB) broth (yeast extract, 5 g/L; tryptone, 10 g/L; NaCl, 5 g/L) supplemented with either 50 g/L of xylose for liquid cultures or 20 g/L of xylose and 15 g/L of agar for a solid medium. Sugars were filter sterilized, and the other ingredients were autoclaved. The strains were stored in glycerol stocks [50% (v/v)] at −80 °C after overnight growth on LB.

The seed culture was inoculated from a newly grown culture of strain K011 grown overnight on a solid medium. The liquid culture was incubated for approximately 24 h at 30 °C with agitation (90 rpm) on a rotary shaker. Cells were harvested by centrifugation (12 000g for 10 min) and resuspended in the sterile basal medium. Each fermentation culture was inoculated with 0.15 mg of cells/mL of medium; an 1.0 optical density at 550 nm was determined to be equal to a concentration of 0.30 mg/mL of cell dry weight (data not shown).

Mini fermentors with automatic pH control were constructed and operated as described previously. Each 500 mL Flecker culture vessel contained 180 mL of neutralized hydrolysate or a similar mixed sugar solution, as a control, supplemented with 20 mL of a 10× basal medium solution (10 g/L of tryptone and 5 g/L of yeast extract) and 0.02% (v/v) antifoam 289 (Sigma, St. Louis, MO). The cultures were incubated at
35 °C and sampled (1.5 mL) periodically for ethanol measurements. The pH set point was maintained by addition of 4.0 N KOH.

Analytical Methods. Ethanol concentrations were measured by gas-liquid chromatography using a Hewlett-Packard 5890A gas chromatograph (Hewlett-Packard Co., Wilmington, DE) equipped with a 80/100 Porapak Q column (6 ft × 1.8 in.; Supelco, Bellefonte, PA) and a flame ionization detector. The injection temperature was set at 200 °C, the oven temperature at 165 °C, and the detector temperature at 250 °C.17

The concentrations of furfural and glucose in solution were measured by analytical liquid chromatography. The analytical system included a 20 cm × 7.8 mm i.d. column packed with Aminex Q15S resin (22 μm particle diameter) operated at 85 °C. Deionized water (1.0 mL/min) was used as the mobile phase. Sample volumes of 50 μL were used. A Waters R401 refractive index detector (Milford, MA) was used to measure elution of furfural and glucose in the solution. The glucose concentrations were confirmed using a Beckman Glucose Analyzer 2 (Beckman, Fullerton, CA).

Results and Discussion

Batch Adsorption. Batch adsorption experiments were run with both resins using furfural solutions with concentrations similar to those found in hydrolysates (0.1–1%). The adsorption behavior at 30, 50, and 70 °C followed a Langmuir adsorption trend (eq 1) for the entire tested range (Table 3), where \( q_0 \) and \( K_T \) are constants assuming a fixed number of adsorption sites with reversible monolayer formation. These results confirm the Langmuir-like isotherms reported by Jerabek et al. for adsorption of furfural at room temperature on styrene and divinylbenzene polymer adsorbents.16

\[
q = \frac{q_0 c}{K_T + c}
\]  

The best equilibrium conditions were achieved at 30 °C, where 90 mg of furfural was adsorbed per gram of dry XAD-4 at an equilibrium solution concentration of 2 g/L of furfural. At the same equilibrium solution concentration of 2 g/L (0.2%), the static loading was 70 and 55 mg of furfural/g of dry resin at 50 and 70 °C, respectively (Table 3).

The trends for the adsorption of furfural to XAD-7 were similar to those for XAD-4. The equilibrium adsorption behavior followed a Langmuir trend for all tested concentrations of furfural (Table 3). At the equilibrium furfural concentration of 3.5 g/L (0.35%), the highest equilibrium loading occurred at 30 °C, where 80 mg of furfural was adsorbed per gram of XAD-7. At 50 and 70 °C, the quantity of furfural adsorbed was 60 and 55 mg/g of dry resin, respectively.

Figure 2 shows the comparison of furfural adsorption to XAD-4 and XAD-7 at 30 °C. The isotherm for XAD-4 is higher than the isotherm for XAD-7 at this temperature. At an equilibrium solution concentration of 2 g/L of furfural, XAD-4 has an equilibrium adsorption of 90 mg of furfural/g of dry XAD-4 compared to approximately 45 mg of furfural/g of dry resin at the same equilibrium solution concentration, 2 g/L.

The results may indicate that the predominant mechanism of attraction between the resin and the furfural is hydrophobic attraction. Because XAD-4 is made of a polystyrene–divinylbenzene copolymer, it is more hydrophobic than the XAD-7 that has a methacrylate backbone. The adsorption isotherms are greater for XAD-4 than for XAD-7 because of the greater hydrophobicity of the resin. These results suggest that these polymeric resins may be able to remove other hydrophobic toxins in lignocellulosic biomass such as (hydroxymethyl)furfural and phenolic compounds from lignin degradation.

Determination of Adsorption Equilibrium Constants. The concentration range of furfural chosen for the batch adsorption experiments corresponds to the concentration of furfural found in the pretreatment
hydrolysate used as a fermentation substrate. The equilibrium data can be used to estimate the time at which the furfural will break through the column. This can be compared to experimental results from passing furfural through a column (Figure 3). Because the inlet concentration increases from zero to 0.5% and adsorption is nonlinear, a shock wave will occur.18 The shock velocity can be determined from the interstitial velocity:

\[
u = \frac{1}{\frac{\Delta q}{\Delta c}}
\]

where \(u_{sh}\) = shock velocity (cm/min), \(v\) = interstitial velocity (cm/min), \(\epsilon_p\) = external void fraction (between particles), \(\epsilon_d\) = intraparticle void fraction (within a particle), \(K_d\) = fraction of interparticle volume species that can penetrate \(= 1.0\), \(\rho_s\) = structural solid density of the XAD-4 resin (g/mL), \(\Delta q\) = change in furfural adsorbed (mg/g of dry resin), and \(\Delta c\) = change in the furfural concentration in an aqueous solution (mg/mL).

A discussion of how local equilibrium theory relates elution profiles of adsorbing or desorbing solutes to its equilibrium isotherm is reviewed by Ladisch.19 \(K_d\) was assumed to be equal to 1 because the intraparticle void fraction is based on the void volume accessible to furfural. Assuming local equilibrium, the \(\Delta q/\Delta c\) term in the denominator is the slope of the chord connecting the points 0.0% and 0.5% on the Langmuir isotherm. With this assumption, a shock velocity of 0.155 cm/min was calculated for the column operating at 30 °C. Knowing the shock velocity, the time for breakthrough can be determined also using the length of the bed, \(L\):

\[t_c = \frac{L}{u_{sh}}\]

where \(t_c\) is the time (min) for the stoichiometric center of the concentration wave to move through the column. The time was calculated to be 355 min. The experimental value for \(t_c\) was about 350 min (shock velocity = 0.16 cm/min). The experimental data closely match the model.

Batch Desorption. Next, the de/adsorption of furfural from the resin was characterized for the stationary phase. Pure solutions of alcoholic solvents, methanol, ethanol, n-propanol, and n-butanol, were used to desorb the furfural from the contacted resins. For all four solvents, greater than 95% of the furfural was removed from both XAD-4 and XAD-7 at 50 °C.

Another factor to consider for the desorption of furfural from the resin is the interaction between the solvent and the resin. At the end of the batch desorption experiments, the resins were washed in water and the resins contacted with n-propanol and n-butanol still had the aroma of the alcoholic solvents associated with them while methanol and ethanol were odorless. The ideal solvents from the four evaluated would be methanol and ethanol because they desorbed the furfural and appeared to have less interaction with the resin than n-propanol and n-butanol.

The conditions for operating the adsorption column were determined from the results of the batch adsorption and desorption studies. The resin chosen for packing the column was XAD-4 because of its higher capacity to adsorb furfural than XAD-7 at the conditions studied. The column temperature was set at room temperature, 25 °C, based upon the inverse correlation of temperature on the adsorption capacity of the resin. Ethanol was chosen as the solvent to desorb furfural from the resin because it desorbed furfural from the resin and did not adsorb to the column as strongly as the longer chain alcohols.

Adsorption Column and Material Balance on Furfural. Two experiments were run with the XAD-4 adsorption column. In the first experiment, a 0.5% furfural solution in water was passed through the column to determine the dynamic adsorption between furfural and the resin. In the second experiment, 0.5% furfural and 0.5% glucose solutions in water were pumped through the column to determine glucose adsorption on the resin and whether the presence of glucose would affect the adsorption of furfural onto XAD-4.

The breakthrough profiles for both experiments, 0.5% furfural in 0.5% glucose and without glucose, are shown in Figure 3. The first component to break through is glucose. Glucose first starts to appear to exit the column at 16 min, which corresponds to approximately the void volume of the packed bed. The breakthrough profile for glucose is sharp, with a concentration of 0.5% being...
of the water wash step. Because approximately 3 g of furfural in the water exiting the column at the end
loading. The quantity of free furfural in the void fraction (Table 4). Between 2.7 and 3.0 g of furfural was adsorbed to 36.1 g of dry XAD-4 resin. This gives a dynamic loading of 0.290 mg of furfural adsorbed/mg of dry XAD-4)

| Table 4. Material Balance of Furfural after Processing through the Adsorption Column at 30 °C |
|-----------------|-----------------|-----------------|
| total furfural  | furfural in water (g) | furfural in 0.5% glucose (g) |
| furfural unadsorbed | 5.1 | 4.9 |
| furfural in the water wash | 3.0 | 2.7 |
| furfural in ethanol | 6.7 | 7.0 |
| furfural adsorbed to the resin (by difference) | 10.3 | 10.4 |
| total furfural accounted for (%) | 96.1 | 95.2 |
| total adsorbed furfural accounted for (%) | 94.5 | 93.3 |
| dynamic loading (mg of furfural adsorbed/mg of dry XAD-4) | 0.290 | 0.290 |

reached at 32 min, approximately two void volumes. The fact that the glucose exits the column after 1 void volume indicates that there is little interaction between glucose and the resin.

The furfural breakthrough profile appears to be very similar for both experiments, furfural with and without glucose (Figure 3). This would indicate that the glucose interaction with the resin was slight enough that it did not interfere with the adsorption of furfural.

In both cases the furfural starts to breakthrough the column around 200–210 min, approximately 12.8 void volumes. The furfural concentration exiting the column reaches 0.5% between 470 and 500 min, between 28.9 and 30.7 void volumes. Nearly 7 void volumes of a furfural-free 0.5% glucose solution was processed before the furfural concentration reached 0.05%.

The total amount of furfural processed in both cases is similar, 15.4 g in water and 15.3 g of furfural in 0.5% glucose (Table 4). The amount of furfural that broke through unadsorbed was 5.1 g in water and 4.9 g in 0.5% glucose. The difference between the quantity adsorbed and unadsorbed indicated that about 10.4 g of furfural was adsorbed to 36.1 g of dry XAD-4 resin. This gives a dynamic loading of 290 mg of furfural adsorbed/g of dry resin for both cases (Table 4). Between 2.7 and 3.0 g of furfural desorbed in the water wash step after furfural loading. The quantity of free furfural in the void fraction was calculated to be 0.5 g based on the concentration of furfural in the water exiting the column at the end of the water wash step. Because approximately 3 g of furfural was desorbed in the first water wash, this may indicate that the desorption in this step was due to a large concentration difference of furfural between furfural in the resin and the relatively furfural-free water.

The majority of furfural was desorbed during the ethanol wash. Between 6.7 and 7.0 g of furfural was removed during this step. The subsequent wash step with water had no furfural, so it was assumed that the furfural was almost completely desorbed in the first water wash and the ethanol wash. The recovery of the adsorbed furfural from both experiments was between 93 and 95%, which would indicate that approximately 20 mg of furfural was irreversibly bound per gram of dry resin. While batch (instead of column) adsorption could be used, recovery, regeneration, and recycle of the adsorbent are necessary because of resin cost. Hence, column operation is preferred over a batch approach.

**Fermentation of Hydrolysates.** The effectiveness of the pretreatment in detoxifying the hydrolysate was tested using ethanologenetic E. coli strain K011.20,21 The strain K011 was chosen for the following reasons: (a) it is one of the few strains that ferment the sugars found in corn fiber hydrolysate (i.e., arabinose, glucose, galactose, and xylose),5,20,21 (b) it produces ethanol yields near the theoretical limit,20,22 and (c) it has been well characterized for lignocellulosic fermentations.20,22,23 Fermentations were run with both pretreated and untreated hydrolysates. As an additional control, a mixture of sugars containing equivalent concentrations of arabinose, glucose, and xylose as the hydrolysate was also fermented. Each fermentation was run in triplicate.

Prior to the fermentation, the hydrolysates were neutralized with Ca(OH)2, filtered, sterilized, and supplemented with yeast extract and tryptone. The fermentations were run in pH-controlled minibioreactors. Progress of the fermentations was followed by measuring the ethanol concentration (Figure 4). No significant ethanol was produced from the fermentations of the untreated hydrolysate, indicating that neutralization did not remove the inhibitors. In contrast, strain K011 fermented the adsorbent-treated hydrolysate nearly as rapidly as the mixed sugars control. Both the adsorbent-treated hydrolysate and mixed sugars control were completed by 80 h and produced equal amounts of ethanol. The ethanol yields for the hydrolysate and mixed sugars fermentations were 0.48 ± 0.03 and 0.42 ± 0.01 g of ethanol/g of sugars, respectively. The final ethanol yields are 94% of the theoretical yield, 0.511 g/g, for the fermented hydrolysate and 82% for the mixed sugar fermentations.17 Therefore, adsorbent treatment was necessary for fermenting the hydrolysate. Additionally, fermentation of adsorbent-treated hydrolysate progressed as rapidly as the mixed sugars fermentation, which was totally free of inhibitors. The ethanol yield was higher for the hydrolysate compared to the mixed sugars fermentation, as has been reported for the fermentation of other hydrolysates by strain K011.17

**Conclusions**

From the results of the adsorption column and the fermentations, polymeric adsorbents are useful and can be used to remove aldehydes, such as furfural, that inhibit fermentations. XAD-4 is an effective polymeric
adsorbent in an adsorption column, separating furfural from the utilizable sugars that can be fermented to value-added products such as ethanol or 2,3-butanediol. The XAD-4 resin is suitable because it has a high specificity for furfural and shows little interaction with glucose. Ethanol is an effective desorption solvent because it is hydrophobic enough to remove the furfural from the resin without strongly interacting with the resin itself. The use of XAD-4 in a packed bed column allows continuous furfural removal from large volumes of hydrolysate liquid and column regeneration utilizing ethanol produced on site.

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