Removal of the Fermentation Inhibitor, Furfural, Using Activated Carbon in Cellulosic-Ethanol Production

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · NOVEMBER 2011

Impact Factor: 2.59 · DOI: 10.1021/ie2013983

5 AUTHORS, INCLUDING:

Kuang Zhang
Georgia Institute of Technology
6 PUBLICATIONS **51** CITATIONS
SEE PROFILE

William Koros
Georgia Institute of Technology
252 PUBLICATIONS **8,126** CITATIONS
SEE PROFILE

I&EC research
Industrial & Engineering Chemistry Research

ARTICLE

pubs.acs.org/IECR

Removal of the Fermentation Inhibitor, Furfural, Using Activated Carbon in Cellulosic-Ethanol Production

Kuang Zhang,[†] Manoj Agrawal,[†] Justin Harper,[†] Rachel Chen,[†] and William J. Koros*[,†]

[†]School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, 778 Atlantic Drive, Atlanta, Georgia 30332-0100, United States

ABSTRACT: Ethanol can be produced from lignocellulosic biomass through fermentation; however, some byproducts from lignocellulosics, such as furfural compounds, are highly inhibitory to the fermentation and can substantially reduce the efficiency of ethanol production. In this study, commercial and polymer-derived activated carbons were utilized to selectively remove the model fermentation inhibitor, furfural, from water solution during bioethanol production. The oxygen functional groups on the carbon surface were found to influence the selectivity of sorbents between inhibitors and sugars during the separation. After inhibitors were selectively removed from the broth, the cell growth and ethanol production efficiency was recovered noticeably in the fermentation. A sorption/desorption cycle was designed, and the sorbents were regenerated in a fixed-bed column system using ethanol-containing standard solution. Dynamic mass balance was obtained after running four or five cycles, and regeneration results were stable even after twenty cycles.

1. INTRODUCTION

Corns and other starch-rich materials can be effectively converted to ethanol by fermentation. This method is mature and easy to control;[1,2] however, the cost of ethanol production is rather high mainly due to the expensive feedstock. As lignocellulosic biomass accounts for about 50% of biomass in the world, there is increasing interest in producing ethanol from lignocellulosics.[3−5] The use of lignocellulosics can not only increase the availability of raw materials greatly for ethanol production but also potentially reduce the production cost considerably. These facts notwithstanding, the production of ethanol from lignocellulosics is more difficult than from starch-rich materials due to its more complex molecular composition. The chemical hydrolysis of lignocellulosic materials used to obtain monosaccharide-rich hydrolysates generally coproduces many different byproducts including furfural and related compounds. Furfural compounds, from pentose degradation, are highly toxic to fermenting species,[6,7] thus negatively affecting the overall wood-to-ethanol conversion process. Other byproducts, such as acetic acid and phenolic compounds, can also inhibit the fermentation. Acetate-resistant strains have been reported to be capable of producing ethanol at high acetate concentration.[8] This research aims to study the elimination of inhibition effect of furfural on fermentation by removing it from the aqueous solution.

To reduce the inhibitor's toxicity during the fermentation, the development of effective removal strategies for these inhibitors from the biomass-pretreated solution is attractive. It is difficult to remove furfural from the hydrolysis solution via distillation due to its high boiling point.[9] Moreover, with dozens of hydrolysates and suspended particles, the composition of the biomass-pretreated solution is very complex, which could easily cause membrane fouling if membrane separation were employed.[10] Adsorption is a convenient and effective technique to remove low concentrations of chemicals from water.[11−15] Activated carbon adsorption is of interest due to its high sorption capacity and cost-effective industrial application. Selective removal of inhibitors is highly desirable during the separation, since valuable hydrolysates, such as monosaccharide and soluble oligosaccharide, should not be removed. These sugars are the source to be converted into ethanol in the fermentation.

Adsorption using activated carbon is studied in this work for inhibitor removal and to determine the selectivity between inhibitor and sugar. We also investigate recovery of bacteria cell growth and ethanol production during fermentation after the inhibitor removal. In addition, a sorption/desorption cycle of sorbent use is considered here. The regeneration of sorbent considered by using low ethanol-containing water solution to desorb the spent sorbent is economically attractive.

2. MATERIALS AND METHODS

2.1. Adsorbates and Adsorbents. The model inhibitor investigated in this work is furfural. Two types of activated carbon were studied as sorbents. Norit_1240 is the commercial activated carbon purchased from Norit Company, and polymer-derived carbon (PF800) is made by pyrolyzing poly furfural at 800 °C under argon atmosphere. Poly furfural is synthesized using furfural as the only monomer, H_2SO_4 as the catalyst, and ethanol as the solvent.

To investigate the impact of carbon surface oxygen groups on the sorption process, a known amount of carbon was oxidized using 60 wt % nitric acid. The reaction mixture was heated to 78 °C, and the reaction was allowed to continue for 6 h. The modified carbon samples are represented by Norit_1240_HNO_3 and PF800_HNO_3, respectively. After oxidation, each modified

Received: June 30, 2011
Accepted: October 10, 2011
Revised: October 5, 2011
Published: November 03, 2011

dx.doi.org/10.1021/ie2013983 | *Ind. Eng. Chem. Res.* 2011, 50, 14055–14060

carbon sample was washed with DI water to eliminate the remaining nitric acid in the sample.

2.2. Characterization of Activated Carbon. The surface morphologies of the carbons were analyzed using a LEO 1530 thermally assisted field emission (T-FE) scanning electron microscopy (SEM) at an acceleration voltage of 3.0 kV or 8.0 kV. Prior to analysis, samples were dried at 100 °C and stored in a desiccator overnight.

The surface chemical composition of the samples was determined by X-ray photoelectron spectroscopy (XPS). The analysis was performed on a Thermo K-Alpha under 5×10^{-10} Pa. The survey scans were collected from 200 to 600 eV with a pass energy of 50 eV. For calibration purposes, the carbon 1s electron bond energy corresponding to graphitic carbon was referenced to 284.5 eV. The samples were dried at 100 °C for 24 h before the analysis.

2.3. Sorption Test. Two activated carbon sorbents were tested for sorption of furfural in batch tests. A small amount of sorbent was added to a plastic-stopper Erlenmeyer flask containing 20 mL of furfural solution (the mass of sorbent to the mass of solution was 1/100), and shaken at 25 °C for a specific time period (usually 10 min) in a shaking water bath (Grand OLS 200 L). The sorption capacity (Q_c) of the furfural was calculated using eq 1

$$Q_c = V_s*(C_o - C_e)/M \quad (1)$$

where Q_c is the equilibrium sorption capacity (mg/g), V_s is the volume of the furfural solution (L), C_o and C_e are the initial and equilibrium concentration of furfural in solution (mg/L), respectively, and M is the mass of sorbent used (g).

The distribution coefficient of furfural K_f, i.e., the ratio of the concentration of adsorbed furfural in carbon to the equilibrium concentration of furfural in the solution, is expressed as eq 2

$$K_f = C_{fc}/C_{fs} \quad (2)$$

where C_{fs} is the equilibrium concentration of furfural in the solution, and C_{fc} is the equilibrium concentration of furfural in carbon calculated with eq 3

$$C_{fc} = (C_o - C_s)*V_s/V_c \quad (3)$$

where $V_c = M/\rho$, is the volume of carbon; M is the mass of sorbent, and ρ is the true density of carbon. This true density was measured as 1.41 kg/L and 1.45 kg/L for Norit_1240 and PF800 respectively with a density gradient column at 30 °C (Techne Inc.). The distribution coefficient of sugar K_s is calculated with the similar method described above.

Another separation performance of the sorbent is measured by its selectivity between furfural and sugar. The selectivity equals to the ratio of the distribution coefficient of furfural and sugar, as expressed in eq 4

$$\alpha_{f/s} = \frac{K_f}{K_s} = \frac{C_{fc}/C_{fs}}{C_{sc}/C_{ss}} \quad (4)$$

where C_{so} is the equilibrium concentration of sugar in carbon, and C_{ss} is the equilibrium concentration of sugar in the solution.

The concentration of furfural was determined with a DU 720 UV−vis spectrophotometer (Beckman Coulter), using a precalibrated curve of UV absorption vs furfural concentration. The concentration of monosaccharide was determined by a Dionex High Performance Anion Exchange Chromatography (HPAEC) with triple pulse amperometry (PAD) detector and a CarboPac PA10 anion-exchange column.

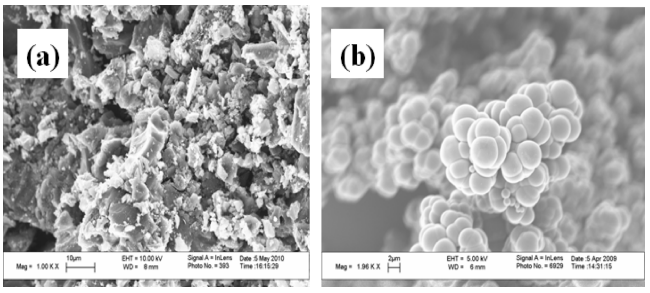

Figure 1. SEM photographs of (a) Norit_1240 and (b) PF800.

2.4. Fermentation with Activated Carbon Treatment. Cultures were grown in the rich medium including 1% (w/v) yeast extract, 0.2 wt % KH_2PO_4 supplemented with 1.2 wt % glucose and 0.4 wt % xylose, and pH was controlled at 5.8. Additionally, furfural was added into broth at 4 g/L concentration, while there was no furfural in the control fermentation. Concentrations of sugars and furfural compounds were chosen so as to be close to those found in switch grass hydrolyzate.[16] All fermentations were carried out with *Zymomonas mobiliz A3*, a recombinant strain from wild-type *Zymomonas mobiliz ZM4*. The fermentations were carried out in 9 mL culture contained in 15 mL screw-cap centrifuge tubes, shaken at 250 rpm. The temperature was controlled at 30 °C. Concentration of ethanol was determined by high performance liquid chromatography (HPLC) with a refractive index detector. Cell density was measured by spectrophotometer.

2.5. Sorption/Desorption Cycle Test. Low ethanol containing water solution was used to desorb furfural from sorbents. The sorption test was investigated with 7.5 wt % ethanol in the solution and compared to the case without ethanol, as described in section 2.3.

Based on the results in batch tests, sorption tests in column system were also investigated. A sorption−desorption regeneration cycle was designed. After biomass pretreatment, a furfural-rich feed goes to a sorption column for furfural removal, followed by the flow of low furfural-containing feed from sorption column to fermentation for ethanol production. After fermentation, the ethanol-containing liquid flows back into the column to desorb the furfural from sorbent. Furfural enriched liquid then goes to distillation to purify ethanol from the solution. After desorption, the regenerated sorbent is ready for the next cycle of sorption−desorption. In our research, the step of fermentation between sorption and desorption was simulated by adding a certain amount of ethanol into the liquid after sorption process to simulate 7.5 wt % ethanol was produced in the fermentation.

3. RESULTS AND DISCUSSION

3.1. Characteristics of Activated Carbon. The morphologies of the carbon samples were investigated with SEM and shown in Figure 1. PF800 is spherical, and its particle size ranges from about 1.5 to about 2.5 μm. On the contrary, Norit_1240 is granular, and its particle size ranges from 0.84 to about 2.38 mm.

The XPS survey spectra of the investigated carbons indicate the presence of two distinct peaks due to carbon and oxygen (Figure 2). The O1s spectra (530−538ev) reveal the presence of oxygen functionalities, such as carbonyl and carboxyl groups, on the carbon samples.[17−20] The intensity of the oxygen peak indicates the entire amount of associated oxygen on the carbon surface. As shown in Figure 2, the oxygen content of sample PF800

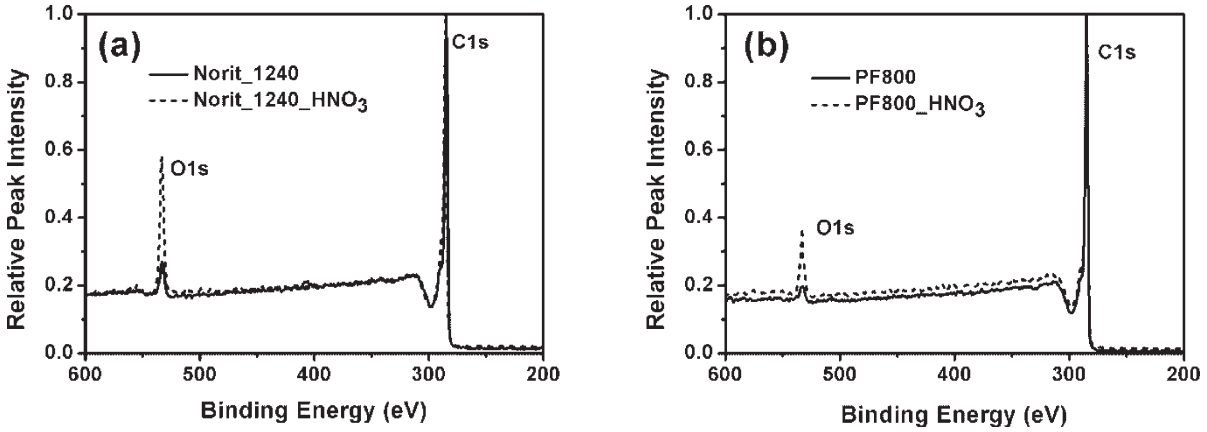

Figure 2. XPS spectra of modified and unmodified samples of (a) Norit_1240 and (b) PF800.

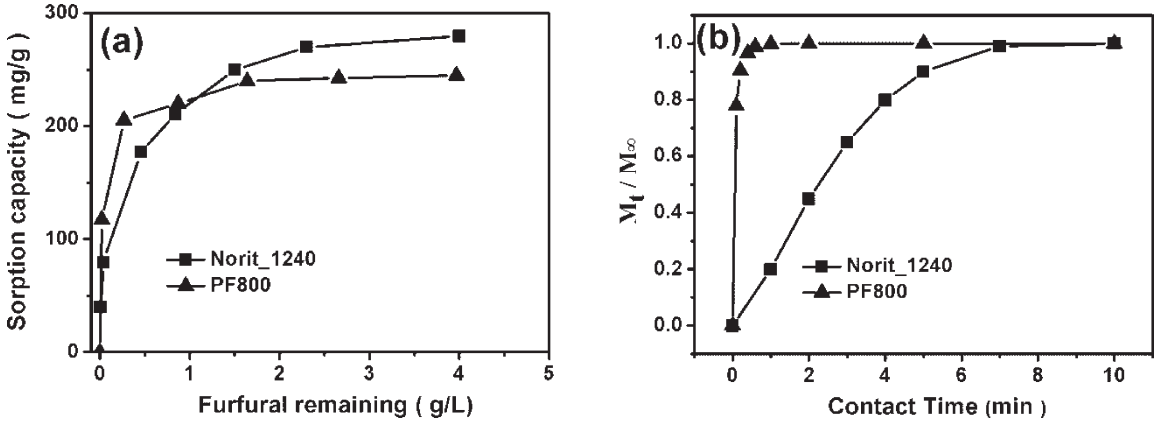

Figure 3. Furfural sorption on carbon samples: (a) sorption capacity and (b) equilibrium time.

is 1%, i.e., much lower than 5% as in the sample Norit_1240. After oxidation with nitric acid, the oxygen content increased clearly as expected on both modified carbon samples, PF800_HNO_3 and Norit_1240_HNO_3 respectively. No presence of peaks in the Nls regions (395−405ev) on the modified carbon indicates that the carbon samples were washed thoroughly after modification and no nitric acid remained on the samples.

Pure carbon is hydrophobic in character. The hydrophobicity decreases, and the carbon becomes more hydrophilic, as the amount of oxygen associated with the carbon surface increases. Therefore, the carbon samples with various oxygen content perform differently in the sorption tests.

3.2. Selective Sorption of Furfural. Under equilibrium conditions, the furfural in sorbent and in residual solution is shown in Figure 3a; both PF800 and Norit_1240 demonstrate large sorption capacity of furfural, but PF800 shows large sorption capacity even at low furfural concentration. This indicates good affinity between PF800 and furfural. The kinetic behavior of furfural sorption in activated carbon is shown in Figure 3b, in a plot of the ratio of M_t/M_∞ as a function of time, where M_t is the amount of furfural adsorbed by the sorbent at the time t, and M_∞ is the saturated sorption amount of furfural by the sorbent. As expected, PF800 shows rapid mass transfer property due to its small powder size. On the contrary, Norit_1240 reaches equilibrium much slower because of its big granular particle size. Adsorption tests were also performed with furfural and hydroxymethylfurfural (HMF, another fermentation inhibitor) coexisting in the liquid. Since furfural and HMF are similar in chemical structure, the adsorption isotherms are similar. The interference of HMF on adsorption of furfural is negligible.

The separation of furfural from sugar containing liquid by activated carbon involves a competitive adsorption process. Selectivity ($\alpha_{f/s}$) between furfural and sugar is a dominant factor in the performance of sorbents for this application. Higher $\alpha_{f/s}$ indicates higher priority of sorption of furfural over sugar. The oxygen functional groups on the carbon surface, such as carbonyls and carboxyls, exercise a profound influence on the surface chemistry and surface properties of activated carbon. Oxygen groups tend to increase hydrophilicity of carbon surface, making the carbon adsorb more hydrophilic sugar, rather than hydrophobic furfural, in the aqueous solution. Therefore, a low $\alpha_{f/s}$ is observed with increasing surface oxygen content. Accordingly, Norit_1240 with 5% oxygen on the surface exhibits lower $\alpha_{f/s}$ (646), compared to PF800 with 1% oxygen and higher $\alpha_{f/s}$ (7321)

$$\text{PF800}: \ \alpha_{f/s} = \frac{K_f}{K_s} = \frac{C_{fc}/C_{fs}}{C_{sc}/C_{ss}} = \frac{4100}{0.56} = 7321$$

$$\text{Norit1240}: \alpha_{f/s} = \frac{K_f}{K_s} = \frac{C_{fc}/C_{fs}}{C_{sc}/C_{ss}} = \frac{4200}{6.5} = 646$$

The inverse relationship between oxygen content and $\alpha_{f/s}$ of carbon is further demonstrated in the cases of oxidized carbon by

dx.doi.org/10.1021/ie2013983 |*Ind. Eng. Chem. Res.* 2011, 50, 14055–14060

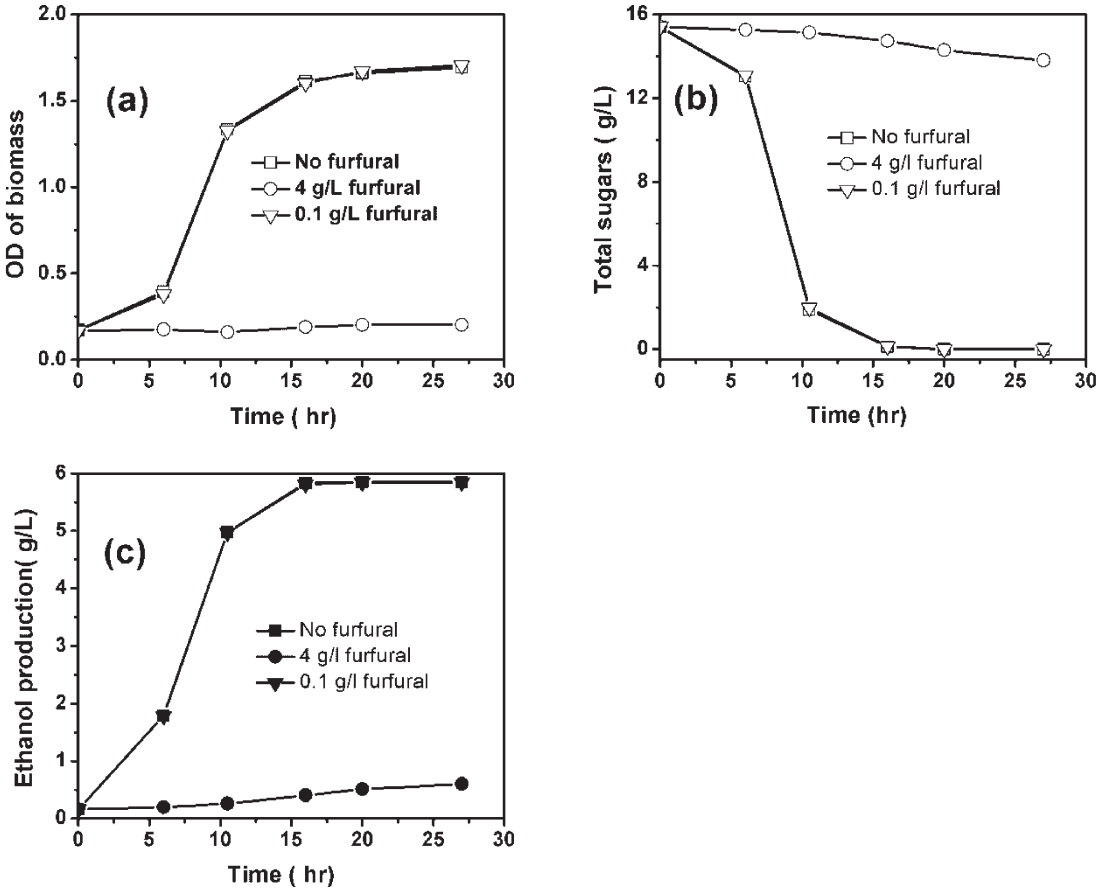

Figure 4. (a) Cell growth, (b) sugar concentration, and (c) ethanol production during the fermentation at different furfural concentrations.

nitric acid, Norit_1240_HNO_3 and PF800_HNO_3 respectively. The $\alpha_{f/s}$ of Norit_1240_HNO_3 drops from 646 to 120 while its oxygen content increases from 5% to 18%, and the $\alpha_{f/s}$ of PF800_HNO_3 drops from 7321 to 510 and its oxygen content increases from 1% to 8%.

Even though the $\alpha_{f/s}$ of Norit_1240 is not as high as PF800, it is still much higher than 1, which indicates Norit_1240 adsorbs furfural preferentially to sugar at the beginning. Only when furfural concentration drops to a low level, Norit_1240 starts to adsorb sugar as well. A further experiment showed that Norit_1240 did not adsorb sugar when there was 1 g/L furfural (and above) existing in the solution, but when the furfural concentration falls below 1 g/L, Norit_1240 adsorbs sugar. Moreover, the sorption capacity of sugar for Norit_1240 can reach 120 mg/g. In comparison, PF800 does not adsorb sugar because of much higher $\alpha_{f/s}$, even when there is only 0.1 g/L furfural remaining in the liquid. Thus, due to the difference of selectivity between Norit_1240 and PF800 the two sorbents can be used in two steps to optimally remove furfural from a water solution. The first step is to reduce furfural content from about 4 g/L, the concentration after biomass pretreatment, to about 1 g/L by using Norit_1240, because the commercial carbon does not adsorb sugar in this range of furfural concentration. The second step is to use PF800 to decrease the furfural content from about 1 g/L to about 0.1 g/L. As a consequence, the majority of furfural (about 75%) could be removed by the commercial carbon, thereby potentially reducing the cost of sorbent in whole and increasing the efficiency.

3.3. Fermentation Improvement by Activated Carbon Treatment. The influence of furfural on the fermentation is shown by the inhibition on cell growth of *Z. mobiliz A3*. Optical cell density results are shown in Figure 4a. An exponential growth was observed without the presence of furfural. As a comparison, when there was 4 g/L furfural in the broth, the cells almost stopped propagating during the fermentation. Consequently, sugar consumption and ethanol production were extremely slow as shown in Figure 4b-c. Therefore, furfural is a strong inhibitor at the level of 4 g/L during the ethanol fermentation of *Zymomonas mobiliz A3*.

The furfural was separated from the broth using the sorbent PF800 and resulted in 0.1 g/L furfural left in the broth after sorption. As shown in Figure 4, the overlapping of the line pertaining to no furfural with the line pertaining to 0.1 g/L furfural indicates that cell growth completely recovered at 0.1 g/L furfural. Also, both sugar consumption and ethanol production completely recovered at 0.1 g/L furfural. No sugar loss was observed after sorption, which was also indicated by no loss of ethanol production. This confirms the high selectivity of the PF800 sorbent.

3.4. Desorption of Furfural and Regeneration of Sorbents. Pure water (the same amount of water compared to the solution in adsorption tests) was utilized to desorb furfural. Only 5% adsorbed furfural was desorbed from the spent sorbents. To improve the regeneration efficiency, different organic solvents were utilized to strip furfural from the spent sorbents, including DMSO (dimethyl sulfoxide), DCM (dichloromethane), TFH (tetrahydrofuran), and ethanol. Although DMSO and DCM were better than other solvents, ethanol was preferred in the

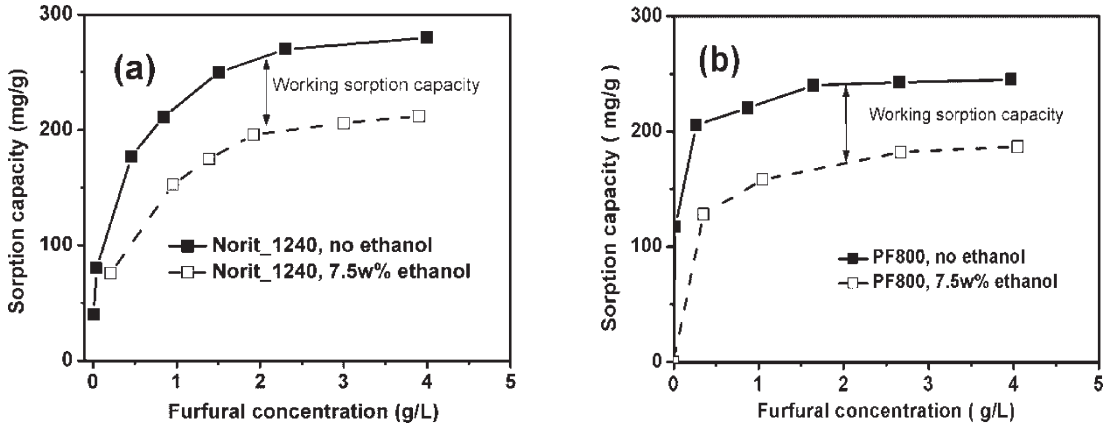

Figure 5. Working sorption capacity of (a) Norit_1240 and (b) PF800 in sorption/desorption cycle.

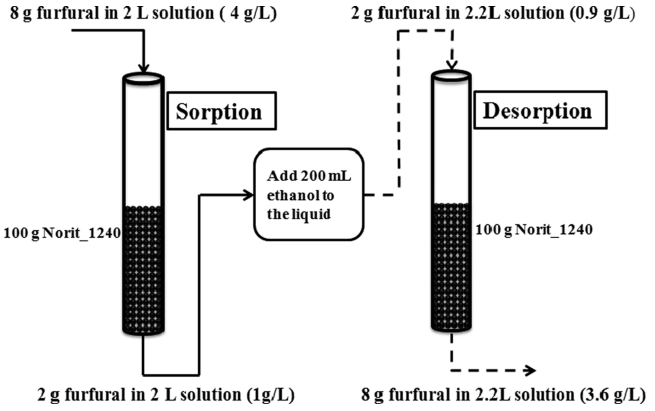

Figure 6. Sorption/desorption cycle of Norit_1240 in column test.

industrial scale due to its lower cost and relative eco-friendliness. Even 7.5 wt % ethanol-containing water solution could desorb a part of furfural from the sorbents. Difference of sorption capacity of furfural was found in sorption tests with and without 7.5 wt % ethanol in the liquid, shown in Figure 5. This difference of sorption capacity is the "working sorption capacity" in the sorption/desorption cycle test in the column system. The working sorption capacity of Norit_1240 for furfural is about 50 mg/g, only one-fifth of the sorption capacity in batch test. Therefore, the mass ratio of sorbent to water solution becomes 1/20 in column system, instead of 1/100 as in the batch test.

The procedure of the column test is shown in Figure 6. Norit_1240 was studied in the column system, because it is granular (8−20 mesh), which is suitable in the column system. The biomass-pretreated liquid, used in the sorption test, was simulated by the water solution with 4 g/L furfural, 1.2 wt % glucose, and 1 wt % xylose. 100 g of Norit_1240 was placed in the column, while 2 L water solution was pumped into the column, according to the mass ratio of 1/20. The flow rate was controlled at 50 mL/min.

After sorption, the furfural concentration was reduced from 4 g/L to 1 g/L. Since 200 mL of ethanol was added into the liquid to simulate 7.5 wt % ethanol produced during fermentation, the furfural concentration became 0.9 g/L before the liquid flew back to the column to desorb furfural from the sorbents. After desorption using 7.5 wt %-ethanol-containing liquid, furfural concentration was enriched to 3.6 g/L, which was less than 4 g/L in the liquid flowing during the sorption process. Although the addition of ethanol lead to a change of furfural concentration, the mass of furfural flowing out the desorption process was still 8 g. Moreover, four or five sorption/desorption cycles are needed before reaching this dynamic mass balance. The results were still stable after running the sorption−desorption cycle 20 times. Meanwhile, the sugars were not removed indicated by HPLC results. Although the working sorption capacity of PF800 is similar to Norit_1240, the small size of powder PF800 caused a water pressure drop in the column system. This problem could be solved by pelletizing PF800. Furthermore, 0.1 g/L furfural could be reached with pelletized PF800 while not losing sugars.

The efficiency of sorbent use could be greatly improved by this regeneration method. Additionally, the presence of furfural in the liquid has no effect on the purification of ethanol by distillation, due to the high boiling point of furfural (161.7 °C). In this research, the ethanol-containing standard solution utilized in the regeneration did not contain acetic acid and other components that could exist in the real fermentation broth. The effect of these components on the regeneration will be investigated in the future research.

4. CONCLUSION

Commercial and poly derived activated carbon samples were utilized to selectively remove furfural from sugar-containing liquid. The oxygen functional groups on the carbon samples significantly influence the sorbent selectivity between furfural and sugar. The fermentation efficiency including cell growth, sugar consumption, and ethanol production recovers clearly after furfural concentration was decreased from 4 g/L to 0.1 g/L. A sorption/desorption cycle method was designed and tested in the column system using low ethanol-containing solution to desorb the spent sorbents. The results indicate a potential application of this regeneration method in the cellulosic ethanol production in industry.

AUTHOR INFORMATION

Corresponding Author

*Phone: 404-385-2845. Fax: 404-385-2683. E-mail: wjk@chbe.gatech.edu.

ACKNOWLEDGMENT

The authors acknowledge the financial support from Chevron Corporation and additional funds from Award no. KUS-I1-011-21

made by King Abdullah University of Science and Technology (KAUST).

REFERENCES

(1) Henke, S.; Bubník, Z.; Hinková, A; Pour, V. Model of a sugar factory with bioethanol production in program sugars(TM). J. *Food Eng.* **2006**, *77*, 416.

(2) Mojovic, L.; Nikolic, S.; Rakin, M; Vukasinović, M. Production of bioethanol from corn meal hydrolyzates. *Fuel* **2006**, *85*, 1750.

(3) Galbe, M.; Zacchi, G. A Review of the production of ethanol from softwood. *Appl. Microbiol. Biotechnol.* **2002**, *59*, 618.

(4) Dien, B. S.; Cotta, M. A.; Jeffries, T. W. Bacteria engineered for fuel ethanol production: current status. *Appl. Microbiol. Biotechnol.* **2003**, *63*, 258.

(5) Petersson, A.; Thomsen, M. H.; Hauggaard-Nielsen, H.; Thomsen, A. Potential bioethanol and biogas production using lignocellulosic biomass from winter rye, oilseed rape and faba bean. *Biomass Bioenergy* **2007**, *31*, 812.

(6) Ranatunga, T.; Jervis, J.; Helm, R.; McMillan, J.; Hatzis, C. Identification of inhibitory components toxic toward zymomonas mobilis CP4(pZB5) xylose fermentation. *Appl. Biochem. Biotechnol.* **1997**, *671*, 185.

(7) Duarte, L.; Carvalheiro, F.; Neves, I. Effects of aliphatic acids, furfural, and phenolic compounds on *Debaryomyces hansenii* CCMI 941. *Appl. Biochem. Biotechnol.* **2005**, *121*, 413.

(8) Jeon, Y. J.; Svenson, C. J.; Joachimsthal, E. L.; Rogers, P. L. Kinetic analysis of ethanol production by an acetate-resistant strain of recombinant *Zymomonas mobilis*. *Biotechnol. Lett.* **2002**, *24*, 819.

(9) Brownlee, H. J.; Miner, C. S. Industrial Development of Furfural. *Ind. Eng. Chem. Res.* **1948**, *40*, 201.

(10) Ghosh, U. K.; Pradhan, N. C.; Adhikari, B. Separation of furfural from aqueous solution by pervaporation using HTPB-based hydrophobic polyurethaneurea membranes. *Desalination* **2007**, *208*, 146.

(11) Ranjan, R.; Thust, S.; Gounaris, C.; Woo, M.; Floudas, C.; Keitz, M.; Valentas, K.; Wei, J.; Tsapatsis, M. Adsorption of fermentation inhibitors from lignocellulosic biomass hydrolyzates for improved ethanol yield and value-added product recover. *Microporous Mesoporous Mater.* **2009**, *122*, 143.

(12) Weil, J. R.; Dien, B.; Bothast, R.; Hendrickson, R.; Mosier, N.; Ladisch, M. Removal of Fermentation Inhibitors Formed during Pretreatment of Biomass by Polymeric Adsorbents. *Ind. Eng. Chem. Res.* **2002**, *41*, 6132.

(13) Lucas, S.; Cocero, M. J.; Zetzl, C.; Brunner, G. Adsorption isotherms for ethylacetate and furfural on activated carbon from supercritical carbon dioxide. *Fluid Phase Equilib.* **2004**, *219*, 171.

(14) Gupta, P.; Nanoti, A.; Garg, M. O.; Goswami, A. N. The removal of furfural from water by adsorption with polymeric resins. *Sep. Sci. Technol.* **2001**, *36*, 2835.

(15) Sahu, A. K.; Srivastava, V. C.; Mall, I.; Lataye, D. Adsorption of Furfural from Aqueous Solution onto Activated Carbon: Kinetic, Equilibrium and Thermodynamic Study. *Sep. Sci. Technol.* **2008**, *43*, 1239.

(16) Franden, M. A.; Pienkos, P. T.; Zhang, M. Development of a high-throughput method to evaluate the impact of inhibitory compounds from lignocellulosic hydrolysates on the growth of Zymomonas mobilis. *Biotechnol.* **2009**, *144*, 259.

(17) Biniak, S.; Szymanski, G.; Siedlewski, J.; Światkowski, A. The characterization of activated carbons with oxygen and nitrogen surface groups. *Carbon* **1997**, *35*, 1799.

(18) Kozlowski, C.; Sherwood, P. X-ray photoelectron spectroscopic studies of carbon fibre surfaces vii-electrochemical treatment in ammonium salt electrolytes. *Carbon* **1986**, *24*, 357.

(19) Xie, Y.; Sherwood, P. X-Ray photoelectron-spectroscopic studies of carbon fiber surfaces. Part IX: the effect of microwave plasma treatment on carbon fiber surfaces. *Appl. Spectrosc.* **1989**, *43*, 1153.

(20) Darmstadt, H.; Roy, C.; Kaliaguine, S. ESCA characterization of commercial carbon blacks and of carbon blacks from vacuum pyrolysis of used tires. *Carbon* **1994**, *32*, 1399.