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Removal of Lignin and Associated Impurities from Xylo-oligosaccharides by Activated Carbon Adsorption

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This paper studies purification with commercial activated carbons of the xylo-oligosaccharides produced by the autohydrolysis of almond shells. Almond shells are agricultural residues with a high content of xylan that are produced abundantly in some regions with a Mediterranean climate. Adsorption equilibrium was measured in a batch system for three commercial activated carbons using a constant concentration of 20 g/L of crude xylo-oligosaccharides and loads of activated carbon from 1.5 to 50.0 mg/mL. Adsorption for lignin-related products was higher than for xylo-oligosaccharides and the selectivity toward lignin adsorption was better when the carbon was highly microporous and had small mesopore diameters, a low volume of mesopores, a low concentration of basic surface groups to limit xylo-oligosaccharide adsorption, and acidic surface groups to favor the adsorption of the lignin-related products. Column tests were performed at a feed rate of crude xylo-oligosaccharide solution of 6.0 mL/min (35 g/L) in columns packed with 22 g of granular activated carbon and operated in up-flow mode. Average retention was around 64% for lignin products and 21% for carbohydrates for the fraction of treated solution collected during the first 2 h of operation (13.1 bed volumes circulated through the bed). Retention for lignin-derived products was limited because part of them is linked to the xylo-oligosaccharides.

Introduction

Xylose-based oligosaccharides (xylo-oligosaccharides or xylo-oligomers) derived from xylan-rich hemicelluloses are carbohydrates with a high potential for novel applications in food and pharmaceutical products. As they are not metabolized by the human digestive system, xylo-oligosaccharides can be used as low-calorie sweeteners and soluble dietary fiber. They act as prebiotics, providing a source of carbon for the development of intestinal microflora and probiotic microorganisms,[1−4] and are already used in fortified foods intended for the development of intestinal microflora.[5,6] In addition, xylo-oligosaccharides have acceptable organoleptic properties and do not exhibit toxicity or negative effects on human health. Ethers and esters prepared from xylan and xylo-oligosaccharides have been synthesized and used as thermoplastic compounds for biodegradable plastics, water soluble films, coatings, capsules, and tablets[7] and also for the preparation of chitosan−xylan hydrogels.[8] Xylo-oligosaccharides extracted by autohydrolysis of bamboo have recently been found to possess a cytotoxic effect on human leukemia cells.[9]

The autohydrolysis of xylan-rich biomass is a suitable process for the production of xylo-oligosaccharides. It eliminates the use of important amounts of the chemicals needed in other extraction processes, such as alkali and acid, and since autohydrolysis takes place in slightly acidic media, many of the side chains in the backbone xylose chains, such as acetyl, uronic acids, and phenolic acid substituents, remain in the xylo-oligosaccharides.[10,11] The differential characteristics of the substituted xylo-oligosaccharides obtained by autohydrolysis have prompted renewed interest in the development of process strategies for achieving a high yield of xylo-oligosaccharides with consistent reproducibility in purity and composition. Though xylo-oligosaccharides are the main component in the nonvolatile products of biomass autohydrolysis, they are mixed with monosaccharides, ferulic acids, uronic acids, and compounds formed by the partial hydrolysis of lignin, the dehydration and degradation of carbohydrates, and condensation reactions. Lignin-derived products are the largest fraction of the impurities associated with xylo-oligosaccharides. Lignin is a three-dimensional polymer made of phenylpropane units linked randomly through alkyl−aryl ether bonds. It acts as a protecting agent and binder in the cell-wall structure of lignocellulosic materials. During autohydrolysis, lignin is depolymerized partially through cleavage of the ether linkages and yields phenolic monomers and oligomers that are soluble in the aqueous media. Also, some of the xylose units in the xylan backbone are bonded to lignin through ether and ester linkages. Consequently, some of the xylo-oligosaccharides contain lignin oligomers linked to the xylose chain. Various impurities from minor constituents of the lignocellulosic biomass—including inorganic salts, extractives, and, in some cases, proteins—are also present.

Clearly, therefore, the crude xylo-oligosaccharides produced by the autohydrolysis of lignocellulosic biomass will contain large amounts of lignin-derived phenolics, carbohydrate dehydration and condensation products, and ash. For instance, the content of xylo-oligosaccharides in the nonvolatile products has been reported to be 58.3% for almond shells,[12] 54.8% for rice husks,[13] and only 46.3% for barley residues.[14] Crude xylo-oligosaccharides must be purified in order to obtain a final product that is well characterized chemically and structurally, homogeneous, repetitive, and suitable for food or pharmaceutical applications. Purification sequences based on liquid−liquid and solid−liquid extractions, solvent precipitation, and ion exchange treatments, as well as combinations of these techniques, have been thoroughly studied.[13,14] Treatment with activated carbon has been shown to be an effective process for removing

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Table 1. Surface Characteristics of the Commercial Activated Carbons (NORIT) Used in This Study

	Activated Carbons		
	AC-1 (ROX 0.8)	AC-2 (PAC 200)	AC-3 (Darco 12 × 40)
S_{BET} (m^2/g)	1024 (1100[a])	1346	616 (650[a])
$V_{0.99}$ (mL/g)	0.625	0.713	0.637
$V_{\alpha,umic}$ (<0.8 nm) (mL/g)	0.152	0.139	0.085
mean pore diam (nm)	2.4	2.1	4.1
iodine number	960 (1000[a])	1060 (900[a])	635 (600[a])
methylene blue (g/(100 g))	22.3 (22[a])	47.0	17.4
pH_{PZC}	8.0	8.7	
Surface Groups (mequiv/g)			
carboxyl	0.2	0.3	0.4
phenolic	4.2	3.0	0.8
lactone	0.1	0.0	0.5
carbonyl	0.5	4.6	0.9
basic groups	2.1	1.2	0.5

[a] Table data provided by NORIT.

impurities from carbohydrate products, having been tested for the detoxification of xylose solutions from the acid hydrolysis of eucalyptus wood before fermentation to xylitol,[15] for the recovery of xylitol from the fermented hydrolyzates of sugarcane bagasse,[16] for the selective recovery of ferulic acid from hydrolyzates of sugar-beet pulps,[17,18] for the separation of maltopentaose from other malto-oligosaccharides,[19] and for the decolorization of sugar solutions[20] and xylo-oligosaccharides.[21] However, so far, there has been no detailed study of the performance of activated carbons for the removal of lignin-derived impurities from crude xylo-oligosaccharide solutions or of the characteristics of the carbons that favor the selective adsorption of lignin-related impurities.

In this paper, we study the performance of three commercial activated carbons for the purification of xylo-oligosaccharides by the selective adsorption of lignin-derived compounds and other impurities. Equilibrium experiments were conducted to obtain the adsorption isotherms, and the results were correlated with the physicochemical properties of the carbons. Continuous adsorption experiments were conducted in a packed-bed column to obtain the breakthrough curves for xylo-oligosaccharides and lignin-derived impurities.

Experimental Section

Materials. Samples of three commercial activated carbons supplied by NORIT (NORIT, the Netherlands) were tested for the purification of the xylo-oligosaccharides: ROX 0.8 (AC-1), PAC200 (AC-2), and Darco 12 × 40 (AC-3). ROX 0.8 is an extruded granular activated carbon used for decoloring starch hydrolyzates and sugars. PAC200 is a powdered carbon used for removing taste, odor, and color from water and industrial process applications. The 12 × 40 carbon is a general-purpose granular carbon grade used in a variety of applications including the purification of fine chemicals and food. For the equilibrium experiments, ROX 0.8 and Darco 12 × 40 were ground and sieved to 0.2 mm, while PAC200 was used directly. In the column tests, all the carbons were used as received. The surface characteristics of the carbons were determined in samples of pulverized carbon according to the methods detailed in the analytical methods section (see also Table 1).

Xylo-oligosaccharides were obtained by the autohydrolysis of grounded almond shells at 179 °C for 23 min. Full details of the reactor system and the operational procedure have been provided elsewhere.[12] Xylo-oligosaccharides from two different reaction batches were used in this study. The first batch comprised solid xylo-oligosaccharides recovered from the autohydrolysis solution by spray drying. This procedure removed water and most of the volatile impurities such as furfural and acetic acid, leaving dry xylo-oligosaccharides (XOs) that still contained all the nonvolatile impurities, such as monosaccharides, organic extractives, lignin-derived phenolics, and inorganic salts. This sample was used for the adsorption equilibrium tests. The second batch comprised an XO solution prepared by autohydrolysis under the same conditions as the first but used directly for the continuous adsorption tests in packed columns. It had a total solids concentration of 35.2 g/L.

Adsorption on Activated Carbon. Adsorption equilibrium was measured in a batch system. A sample of the xylo-oligosaccharides of the first reaction batch recovered by spray drying was dissolved in deionized water at a concentration of 20 g/L. Aliquots of 10 mL of this solution were placed in 20 mL test tubes, and the appropriate amount of activated carbon was added (from 15 to 500 mg). The tubes were capped and placed in a water bath at 30 °C, attached perpendicularly with clamps to a horizontal revolving shaft that had a rotating speed of 2 rpm. After 24 h, the tubes were removed from the bath and the mixture was centrifuged at 4000 rpm for 20 min to precipitate the activated carbon. A sample of the supernatant liquid was filtered through a 0.22 μm nylon syringe filter, placed in an encapsulated HPLC vial, and stored at 5 °C until analysis.

Column tests were performed at room temperature (21 ± 1 °C) using around 22 g of granular activated carbon packed on a 55 mL column, with an inner diameter of 20 mm, made of metacrylate tube and PVC fittings. Activated carbon was submerged in boiling water for 15 min to remove air and fine particles and then extracted and poured immediately into the column, which had previously been filled with water to avoid entrapping air in the carbon bed. The column had wire mesh plates at both ends to prevent the entrainment of carbon particles and was operated in up-flow mode to reduce channeling. The solution of crude xylo-oligosaccharides from the second reaction batch was fed at 6 mL/min with a Watson-Marlow 313F peristaltic pump (Watson-Marlow Bredel, USA), which led to a residence time of 0.15 h. At the end of the experiment, the feed was switched to deionized water for 1 h to clean the column. The product was collected in four fractions—from 0 to 2 h (F1, 13.1 bed volumes circulating through the column), from 2 to 4 h (F2, 26.2 bed volumes), from 4 to 5.5 h (F3, 36 bed volumes), and the washing solution—and the dissolved solids in each fraction were recovered by lyophilization. Also, samples of 2 mL were withdrawn from the outlet stream throughout the experiment, filtered through a 0.22 μm nylon filter, and analyzed by gel permeation chromatography/high-performance liquid chromatography (GPC/HPLC) to determine the instantaneous composition of the product stream, as described below.

Analytical Methods. The surface area and porosity of the activated carbons were determined from their nitrogen adsorption−desorption isotherms obtained at 77 K in an ASAP 2020 surface analyzer (Micromeritics, USA). The samples were previously degassed at 523 K for several hours. N_2 adsorption data for P/P_0 from 10^{-5} to 0.99 were analyzed according to (i) the BET method[22] for calculating the specific surface area, S_{BET} and (ii) the α_S method[23] using Carbopack F Graphitized Carbon Black as reference material to calculate the ultramicromicropore volume[24] (pore diameter < 0.8 nm), $V_{\alpha,umic}$. The total pore volume, $V_{0.99}$, was calculated from nitrogen adsorption at a relative pressure of 0.99. The average pore diameter was calculated from the total pore volume and the surface area with eq 1. The point of zero charge (PZC) was determined by mass titration.[25] Various amounts of activated carbon were added to

a 10 mL solution of 0.1 M NaCl to obtain mixtures with 0.05, 0.1, 0.5, 1.0, and 10% of carbon by weight. The bottles were sealed to eliminate any contact with air and stirred overnight. The equilibrium pHs of the suspensions were measured after 24 h of contact time. The PZC value of the activated carbon was taken as the equilibrium pH of the suspension with the highest concentration of carbon when the change in pH with carbon concentration was low. Methylene blue ($C_{16}H_{18}ClN_3S \cdot 2H_2O$, MB) serves as a model compound for checking the adsorption of medium-size organic molecules from aqueous solutions. A 50 mL portion of a 3.2 mM solution of MB (Scharlau Chemie, Spain) and approximately 50 mg of activated carbon were used in adsorption experiments. The solutions were stirred overnight and filtered to remove the activated carbon in suspension before analysis. The equilibrium concentration of MB in the solution was measured by spectrometry at 664.8 nm in a Dinko Instruments 8500 spectrometer (Dinko Instruments, Spain). The amount adsorbed was calculated from the change in concentration of the solution. The iodine number was provided by NORIT. The oxygenated acid surface groups were determined according to the method of Boehm,[26] and the basic groups were determined by titration with hydrochloric acid. A 25 mg portion of carbon was mixed with 25 mL of each of the following solutions: 0.1 N sodium hydroxide, 0.1 N sodium carbonate, 0.1 N sodium bicarbonate, 0.1 N sodium ethoxide, and 0.05 N hydrochloric acid. The vials were sealed and stirred for 48 h, and the solutions were filtered. Samples of 5 mL were taken. These were titrated with 0.05 N HCl or 0.1 N NaOH to determine the excess of base or acid, respectively. The number of acidic sites of each type was calculated under the assumptions that sodium ethoxide neutralizes all the acidic groups (i.e., the carboxylic, phenolic, lactonic, and carbonyl groups), that NaOH neutralizes the carboxylic, phenolic, and lactonic groups, that Na_2CO_3 neutralizes the carboxylic and lactonic groups, and that $NaHCO_3$ neutralizes only the carboxylic groups. The number of surface basic sites was calculated from the amount of HCl consumed by the activated carbon.

$$\bar{d}_p = 4\frac{V_{0.99}}{S_{BET}} \quad (1)$$

Solid xylo-oligosaccharides were analyzed for their ash content (ASTM D 1102-84 standard method) and for carbohydrates, acetyl groups, and lignin. A sample was dissolved in deionized water and analyzed (i) by HPLC to quantify the free monosaccharides (glucose, xylose, and arabinose), acetic acid, furfural, and hydroxymethyl furfural (HMF) and (ii) by HPLC/GPC to determine the molar mass distribution. Another sample of the XOs was dissolved in 4% sulfuric acid and was quantitatively hydrolyzed at 120 °C for 45 min to convert the oligosaccharides into their constitutive monomers. The hydrolyzate was analyzed by HPLC, and the amount of xylo-oligosaccharides was estimated from the monosaccharides and acetic acid liberated by the quantitative hydrolysis. Lignin was measured as the insoluble residue after the quantitative hydrolysis (Klason-type lignin) by the TAPPI UM 250 method for the acid-soluble lignin. The XO solution from the autohydrolysis reactor (2nd batch of XO) was analyzed with the same procedures. HPLC analyses were performed with a Bio-Rad HPX 87H column at 30 °C (Bio-Rad Laboratories, USA) in an Agilent 1100 series chromatograph (purchased from Agilent, Barcelona, Spain). The solvent was 0.005 M H_2SO_4 at a flow rate of 0.5 mL/min. An Agilent 1100-DAD ultraviolet (UV) diode-array detector and an Agilent 1100-RID refractive index (RI) detector were connected in series. The UV detector was used to quantify furfural and HMF in the samples that contained low concentrations of these compounds. The RI detector was used for the samples with high concentrations of furfural and HMF and for carbohydrates. The molar mass distribution of the xylo-oligosaccharides was determined by GPC using the same chromatograph and the GPC add-on of the LC Chemstation software (purchased from Agilent, Barcelona, Spain). The analyses were performed with a TSKGel G3000PWXL column (Toso Haas, purchased from Teknokroma, Barcelona, Spain) at 25 °C using 0.5 mL/min of a 0.05 mol/L solution of KNO_3 with 83 mg of sodium azide as solvent and the refractive index detector. The system was calibrated with xylose, glucose, and low-polydispersity standards of malto-oligosaccharides and dextrans (Fluka). In all cases, the samples were filtered through a 0.22 μm nylon syringe filter prior to HPLC analyses.

Results and Discussion

Adsorption Equilibrium Tests. Adsorption equilibrium tests were developed using a sample of crude xylo-oligosaccharides obtained by spray drying of the hydrolysis liquor (batch 1). This sample comprised 58.3% xylo-oligosaccharide, 5.0% monomer products (2.4% xylose, 1.5% arabinose, 0.78% glucose, 0.27% HMF, and trace amounts of acetic acid and furfural), 4.8% ash, and 16% Klason-type lignin. The remaining 14.9% of the solid was made up of compounds from the almond shells that were solubilized during the autohydrolysis reaction, e.g., extractives, low molar mass phenolics from lignin, and byproducts from the degradation and condensation of monosaccharides and furfural, which were not identified with the analytical procedures we used.

The adsorption of the carbohydrate and lignin-derived fractions of the xylo-oligosaccharides on activated carbons was tested at 30 °C using a constant concentration of crude xylo-oligosaccharides of 20 g/L in deionized water and concentrations of activated carbon of 1.5, 3.3, 10.0, 16.7, 30.0, and 50.0 g_{AC}/L. Figure 1 shows the GPC chromatograms of the feed solution. The UV signal at 254 nm was attributed to the presence of compounds derived from lignin and extractives and from their condensation with furfural, HMF, and other carbohydrate-degradation products, which accounted for around 30% of the mass of the sample. We assumed that the signal of the refractive index detector was caused mainly by carbohydrates and inorganic salts (soluble ashes), since they constituted nearly 70% of the mass in the crude xylo-oligosaccharides, though all the species in the mixture contributed to the signal of this nonselective detector. The retention times for narrow standards of dextran, malto-oligosaccharides, and xylose are included in Figure 1 for comparison. The RI signal shows that the xylo-oligosaccharides had a molar mass below 50 kDa. The most abundant species had a molar mass of between 1 and 5 kDa. There was also a small fraction of the mixture with a molar mass of below 0.15 kDa (xylose). Some of this was inorganic salts (ashes) that eluted after monosaccharides in this chromatographic system. Data from the UV signal revealed two important facts. First, a significant amount of lignin-derived products eluted at the same interval of retention time as did the xylo-oligosaccharides. This was in agreement with the existence of phenolic side groups such as ferulic acids and lignin fragments, which are directly attached to the xylan backbone chains.[27] Second, almost half of the lignin-derived products were eluted at a retention time that was well above that of xylose (0.15 kDa). These products were low-molar mass phenolics that eluted from the chromatographic column with a different pattern from that of oligosaccharides, partly because they may have

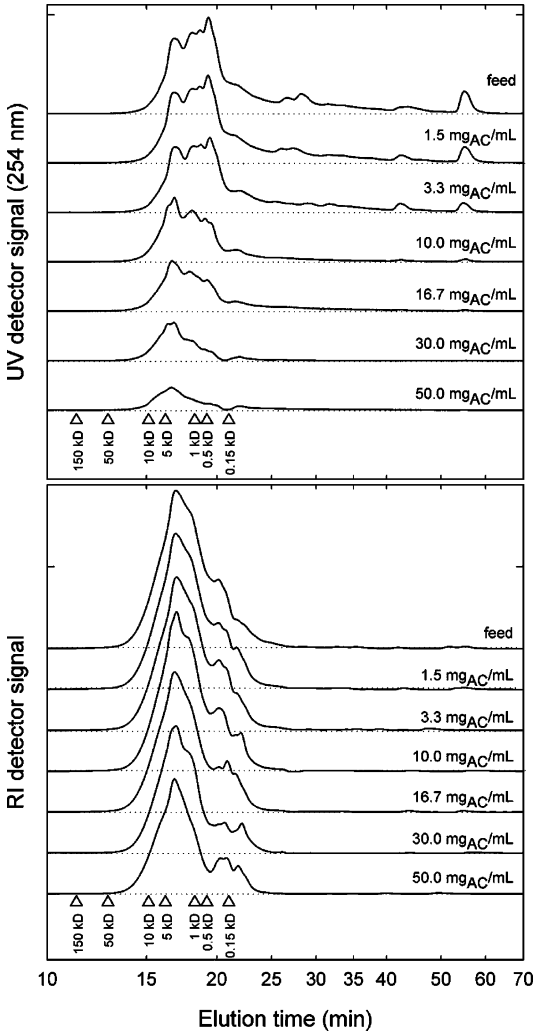

Figure 1. GPC chromatograms (time in log scale) for the xylo-oligosaccharides remaining in solution in the equilibrium adsorption experiments at 30 °C and different loads of the AC-1 activated carbon. The UV signal at 254 nm (top) is caused by lignin-derived phenolics, while the refractive index signal (bottom) is mainly attributed to carbohydrates (oligomers and monomers).

hydrodynamic volumes in 0.05 mol/L KNO_3 that are lower than those of carbohydrates of equivalent molar mass, but mainly because of adsorption on the gel of the GPC column, which increases the elution time. Palm and Zacchi[28] observed the adsorption of lignin-derived compounds from wood autohydrolysis on the gel of filtration columns.

Figure 1 also shows the GPC chromatograms for selected samples of the xylo-oligosaccharide solution treated with AC-1. The low molar mass lignin-derived products, which have the longest elution times in the GPC system, are preferentially adsorbed when small amounts of activated carbon are added to the solution. Figure 1 shows that they were completely adsorbed when 16.7 g_{AC}/L was used. The lignin-products in the range of the elution time of oligosaccharides were also adsorbed, but they were still detected even at 50 g_{AC}/L since they are linked to xylose in xylo-oligosaccharides. The adsorption of the carbohydrate fraction was less significant. Below a carbon load of 16.7 g_{AC}/L, only species with a molar mass of below 0.5 kDa were adsorbed. At a higher carbon load, there was a reduction in the signal of the sample at all molar masses, but even at 50 g_{AC}/L, the total amount of carbohydrates adsorbed was still below 40%. The same qualitative trends were observed for the other activated carbons we tested.

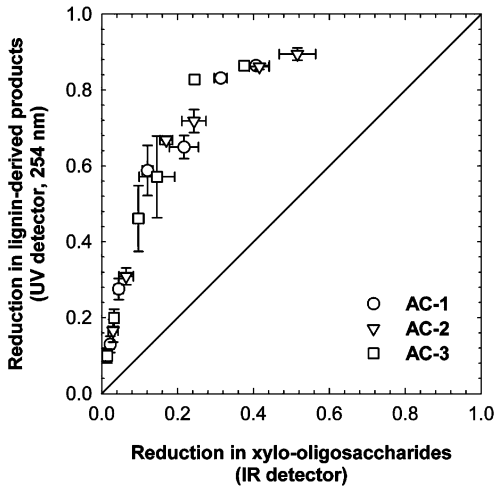

Figure 2. Relation between the reduction in the concentrations of lignin-derived phenolics and carbohydrates at equilibrium for various loads of activated carbon at 30 °C. Error bars are confidence intervals at the 95% probability level.

The reductions in the concentrations of lignin-derived products and carbohydrates (rd_j) were calculated from the areas of the GPC chromatograms by assuming constant response factors (eq 2), and the amounts of each solute adsorbed were calculated from a mass balance for the batch system using eq 3, in which j indicates lignin-derived products or carbohydrates, $C_{0,j}$ (g/L) is the concentration of solute in the feed, $C_{e,j}$ (g/L) is the equilibrium concentration of species j in the solution, $C_{Se,j}$ (g/g_{AC}) is the concentration of solute j adsorbed on the activated carbon at equilibrium, m is the mass of activated carbon (g_{AC}), and V is the volume of the solution (L). Figure 2 shows the reduction in the concentrations of lignin-derived products and xylo-oligosaccharides in solution for the three activated carbons we tested. Lignin-derived products were preferentially adsorbed over the carbohydrate fraction, especially at low concentrations of AC when the low molar mass aromatics were adsorbed. For instance, when 70% of the lignin-derived compounds were adsorbed, around 80% of the carbohydrates were still in solution. When over 80% of these compounds were adsorbed, the adsorption of carbohydrates dramatically increased.

The adsorption of mixtures of organic solutes onto activated carbons is a complex process that is determined by the chemistry of the carbon surface, the interactions between the solutes and the surface, the interactions of the solutes with the solvent, and those of the solvent with the carbon surface. The molar mass of the solute and the distribution of pore diameters of the carbon also play a significant role in determining the fraction of carbon surface that is actually accessible to a specific solute. The preferential adsorption of lignin-derived species over xylo-oligosaccharides may be attributed to several factors. Lignin-derived species are substituted phenolic monomers and oligomers that are more hydrophobic than carbohydrates. Xylo-oligosaccharides will therefore be more stable in water solution than lignin-derived products especially if, as in activated carbons, the surface of the adsorbent is predominantly hydrophobic.

Average pore diameters were 2.4, 2.1, and 4.1 nm for AC-1, AC-2, and AC-3, respectively. Table 2 shows that the activated carbons had a significant fraction of micropores, while Figure 3 shows that the pore volume distribution, which was calculated with the density functional theory (DFT) model,[29] was different for the three carbons. Most of the mesopore volume in the AC-1 carbon corresponded to pores with diameters from 2 to 10 nm, and the rest corresponded to large mesopores (30−50 nm). The

Table 2. Freundlich Isotherms: Results for the Adsorption of the Carbohydrate Fraction and the Lignin-Derived Products on Commercial Activated Carbons[a]

	AC-1 (ROX 0.8)	AC-2 (PAC200)	AC-3 (Darco 12 × 40)
	Xylo-oliogosaccharides		
n	1.00 ± 0.13	0.81 ± 0.11	0.66 ± 0.09
$K_{XO}[L^{(1/n)}/(g_{AC}g^{((1/n)-1)})]$	0.0148 ± 0.0046	0.0324 ± 0.0084	0.0249 ± 0.0054
	Lignin-Derived Products		
n	0.82 ± 0.06	0.82 ± 0.05	0.62 ± 0.05
$K_{LP}[L^{(1/n)}/(g_{AC}g^{((1/n)-1)})]$	0.145 ± 0.008	0.184 ± 0.009	0.134 ± 0.007

[a] Confidence intervals were calculated at $\alpha = 0.05$.

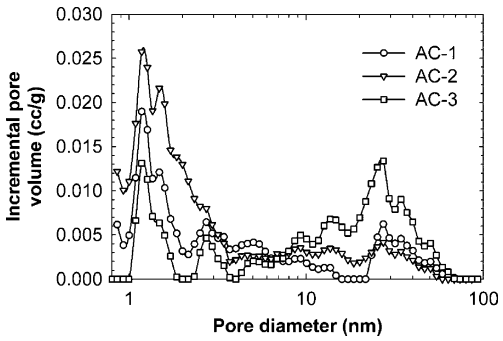

Figure 3. Pore volume distributions for the three activated carbons used in this study.

AC-2 carbon had the largest mesopore pore volume, but it had more pore volume than the AC-1 in the zone of small mesopores and a similar amount of large mesopores. Finally, the AC-3 carbon had very low volume in the small mesopore region, and most of its mesopore volume corresponded to large pores, from 10 to 50 nm. Around half of the lignin-derived compounds and associated impurities that are present in the crude xylo-oligosaccharides had a low molar mass (i.e., around 0.1 kDa) and were easily adsorbed in the three activated carbons, since their entire surface was accessible to these small solute molecules. On the other hand, xylo-oligosaccharides and some of the lignin-derived impurities had molar masses from 1 to 50 kDa, which is roughly equivalent to an interval of molecular diameters from 2 to 10 nm. The area available for the adsorption of the oligomers was therefore dependent on their molar mass: the larger the molar mass, the lower the area they could access. This effect should be more important for carbons AC-1 and AC-2, which have a significant fraction of pores below 10 nm.

However, solute size and the pore diameters are not the only variables governing adsorption. If we compare the GPC chromatograms in Figure 1 for xylo-oligosaccharides and lignin products at a high concentration of carbon AC-1, we can see that the reduction in the concentration of high molar mass solutes was much greater for the lignin products than for xylo-oligosaccharides. The presence of carboxylic and other acidic groups on the surface of the carbon has a definite effect on the adsorption of phenol, since it favors the chemisorption of phenol but hinders physisorption.[31] We may expect the same to be true for the lignin-drived phenolics present in the crude xylo-oligosaccharides. Finally, electrostatic interactions between charged solutes and the surface of the carbon must also be considered. The pH of the xylo-oligosaccharide solution was 5.7 due to the dissociation of the acetyl groups in the backbone chain of the xylo-oligosaccharides and the carboxyl groups in ferulic acids and in some lignin-derived products. Since this pH is below the pH of zero charge of the activated carbons ($8 < pH_{PZC} < 8.7$), we can expect the surface of the carbons to have a positive charge distributed among the basic superficial groups.[31] This should create favorable electrostatic interactions between the positive surface and the negatively charged solutes such as the xylo-oligosaccharide chains that contain dissociated acetyl groups.

$$rd_j = 1 - \frac{C_{e,j}}{C_{0,j}} \tag{2}$$

$$C_{Se,j} = \frac{V}{m}(C_{0,j} - C_{e,j}) \tag{3}$$

$$\ln C_{Se,j} = \ln K_j + n_j \ln C_{e,j} \tag{4}$$

Regardless of the complexity of the phenomena involved in the competitive adsorption of mixtures of polydisperse oligomers with dissimilar chemical structures, simple models can provide some insight into the factors that have a determining influence on the selective adsorption of lignin-related species over xylo-oligosaccharides. Adsorption equilibrium was modeled through the Freundlich isotherm, which relates the concentration of a j solute at equilibrium ($C_{e,j}$) to the concentration of j adsorbed on the surface ($C_{Se,j}$). The unit-capacity parameter, K_j, is a measure of the degree of strength of adsorption, and n_j, the site-energy parameter, is an indication of the heterogeneity of the surface adsorption sites. The closer the value of n_j is to unity, the more homogeneous is the energy of the surface sites. The Freundlich isotherm was linearized to calculate the constants n_j and K_j (eq 4). Figure 4 shows the linearized isotherms, and Table 2 shows the best-fit values of n_j and K_j for the three activated carbons and their confidence intervals at 95% probability. Calculations were done using the robust linear regression algorithm implemented in the *robustfit* function of the statistics toolbox of MATLAB (MathWorks Inc., USA). The isotherm provided an acceptable description of the adsorption of both the lignin-derived products and carbohydrates for the three activated carbons, since the model predictions fell within the scattering of the experimental data.

Possible correlations between the main properties of the activated carbons and the parameters of the Freundlich equation for xylo-oligosaccharides and lignin-derived products were analyzed. Figure 5 shows that the unit-capacity parameter for xylo-oligosaccharide adsorption (K_{XO}) increased with the mesopore volume of the activated carbon, while the site-energy parameter increased linearly with the concentration of basic surface groups. The carbons with more developed mesoporous structures had more surface area available for the adsorption of xylo-oligosaccharides with larger molar mass, thus giving higher values for the unit-capacity parameter of the Freundlich isotherm. Also, the higher the number of basic surface groups on the surface, the stronger the electrostatic interactions between the dissociated acetyl groups of the xylo-oligosaccharide chains and the positively charged surface, thus increasing the site-energy parameter n_{XO} for xylo-oligosaccharides adsorption. The K_{LP} parameter for the lignin-derived phenolics grew with the total concentration of acidic superficial groups. In studies on

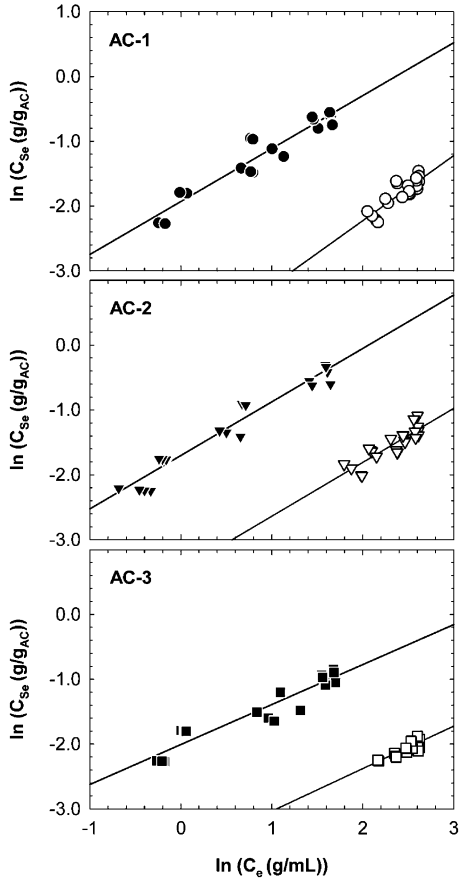

Figure 4. Freundlich isotherms for the adsorption of lignin-derived phenolics (open symbols) and xylo-oligosaccharides (solid symbols) on the three activated carbons at 30 °C.

phenol adsorption from acidic water solutions, the increase in the unit-capacity parameter with the concentration of acidic surface groups has been explained by the existence of two parallel routes: physical adsorption and acid-catalyzed chemisorption.[30] We may expect the contribution of chemisorption to the overall adsorption of the low molar mass phenolics present in the complex mixture of lignin-related products to become more important as the number of acidic surface groups increases, thus increasing K_{LP}. In contrast, the site-energy parameter, n_{LP}, did not have a clear correlation with the concentration of acidic surface groups. Promoting the surface acidic groups by oxidation of an activated carbon reduces the adsorption of phenol from aqueous solution.[31] More acidic groups should favor chemisorption, but they lower physical adsorption because the acidic groups act as electron acceptors and lower the π-electron density in the carbon planes, thus decreasing the interaction between the aromatic rings and the carbon basal planes. Since physical adsorption is the dominant mechanism, the overall consequence is lower phenol adsorption and a decrease in the site-energy parameter, n, of the Freundlich isotherm.[30] In our case, it seems that n_{LP} increased for activated carbons with more acidic surface groups, though the values of n_{LP} for AC-1 (0.82 ± 0.06) and AC-2 (0.82 ± 0.05) were statistically the same even if they had different concentrations of acidic surface groups (6.0 mequiv/g for AC-1 and 7.9 mequiv/g for AC-2). This behavior may be caused by the different nature of the predominant acidic groups in each carbon, which were manufactured from a variety of raw materials using different methods of activation. Phenols are the main acidic group in AC-1 (4.2 mequiv/g), while in AC-2 the main group is carbonyls (4.6 mequiv/g). The relative importance of the chemisorption and physical adsorption paths will therefore be different in each carbon due to the different acidity of these groups. Finally, no direct correlations of the Freundlich parameters with other properties of the activated carbons such as the surface area or the total pore volume were observed.

On the basis of the analysis of the Freundlich isotherms, the purification of xylo-oligosaccharides will require activated carbons with unit-capacity and site-energy parameters that are low for xylo-oligosaccharides and high for lignin-derived products. The AC-1 carbon, with a K_{LP}/K_{XO} of 9.8 ± 3.6, had a slightly better ratio of unit-capacities than AC-2 (5.7 ± 1.8) and AC-3 (5.4 ± 1.4), while the ratio n_{LP}/n_{XO} did not present significant differences due to the large scattering of the results (0.82 ± 0.17 for AC-1, 1.01 ± 0.20 for AC-2, and 0.94 ± 0.20

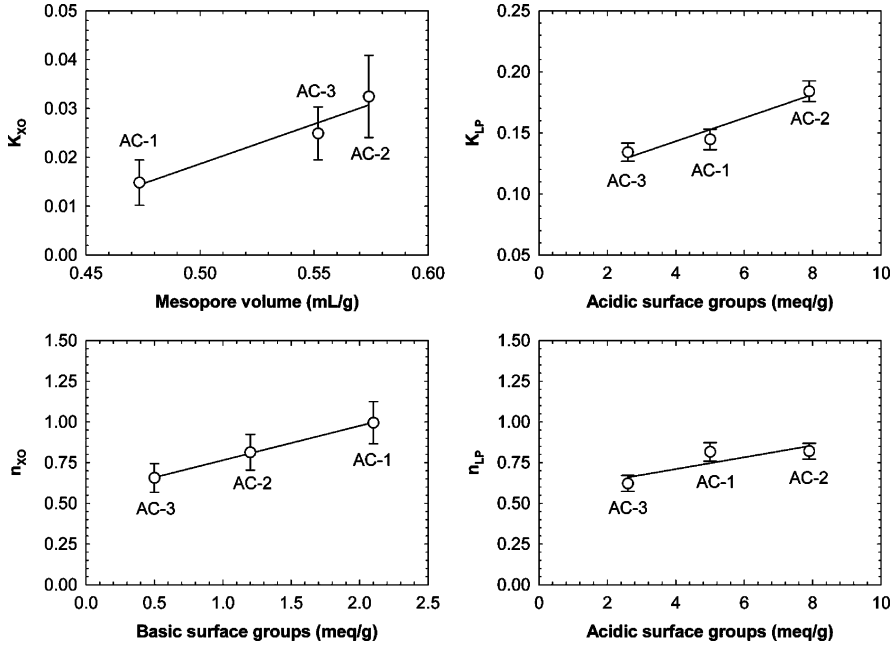

Figure 5. Variation in the constants of the Freudnlich isotherms of lignin-derived compounds and xylo-oligosaccharides (K_{LP}) with the surface properties of the activated carbons. The lines only indicate trends.

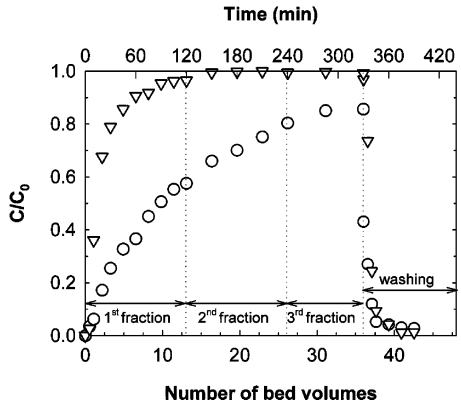

Figure 6. Adsorption of the crude xylo-oligosaccharides from reaction batch 2 on an AC-1 activated carbon column: breakthrough curves for carbohydrates (▽) and lignin-derived products (○).

for AC-3). In general, a suitable activated carbon should have small mesopore diameters, a low volume of mesopores, and a low concentration of basic surface groups to limit xylo-oligosaccharide adsorption. It should also be highly microporous and have acidic surface groups to favor the adsorption of the lignin-related products (high K_{LP}).

Column Tests. Column tests were performed with the ROX 0.8 granular activated carbon (AC-1). This carbon was selected because of its slightly better selectivity toward lignin adsorption and because it was readily available in granular form and more suitable for column packing than AC-2 and AC-3. The latter contained fines and caused problems during operation due to the entrainment of carbon particles and because it led to larger pressure drops across the bed. Figure 6 shows the breakthrough curves for an experiment performed using the second batch of xylo-oligosaccharides solution directly. The solution was fed at 6.0 mL/min, and a column loaded with 22.0 g of activated carbon was used. The activated carbon was rapidly saturated with carbohydrates. Retention for carbohydrates was only 10% after 60 min (6.55 bed volumes circulated), while retention for lignin-derived products was over 60%. After 180 min (19.6 bed volumes), the column was completely saturated with carbohydrates and retention was 0.2% but it was still 30% for lignin products. Figure 7 shows the GPC chromatograms for samples of the effluent taken at selected times during the experiment. The lignin-derived products of low molar mass were completely adsorbed on the column during the first 45 min of the experiment, which corresponds to 4.91 bed volumes of feed circulated through the column, but the high molar mass fraction of lignin products associated to carbohydrates was not adsorbed completely even when the volume circulated was small (2.18 bed volumes). The carbohydrate fraction had low adsorption, and there were few differences in the degree of adsorption with molar mass. The fraction collected during the cleaning of the carbon bed with deionized water contained both carbohydrates and lignin-derived species. The latter were detected in the washing stream even after 60 min of cleaning (6.55 bed volumes of water), which suggests that they were strongly adsorbed on the surface of the carbon.

The fractions collected during the experiment were lyophilized to recover the xylo-oligosaccharides (F1, 0−2 h; F2, 2−4 h; F3, 4−5.5 h; F4, washing, 5.5−6.5 h). The dry product was weighed to calculate the yield and analyzed for ash, klason lignin, monomers, xylo-oligosaccharides, and the molar mass distribution. Table 3 shows that the average concentration of nonvolatile soluble products decreased from 35.2 g/L in the feed to 25.2 g/L in the product collected from the column outlet

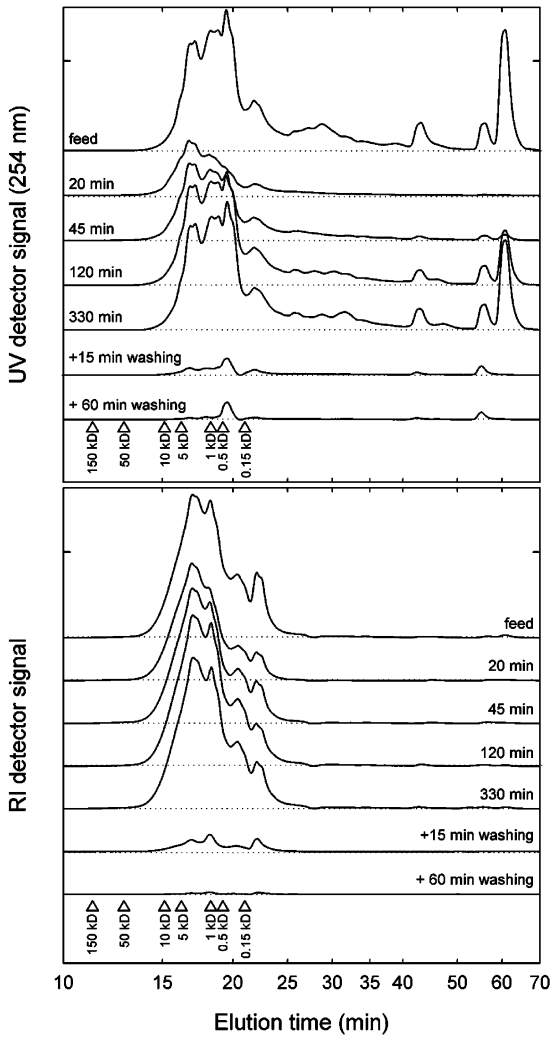

Figure 7. Adsorption of the crude xylo-oligosaccharides from reaction batch 2 on an AC-1 activated carbon column: GPC chromatograms (time in log scale) for the xylo-oligosaccharides remaining in solution. The UV signal at 254 nm (top) is caused by lignin-derived phenolics, while the RI signal (bottom) is mainly attributed to carbohydrates (xylo-oligosaccharides and monomers).

during the first 2 h of the experiment. Analysis of the recovered product shows that monosaccharides and xylo-oligomers were partially adsorbed on the carbon, but the highest adsorption was for lignin-related products and for furfural and HMF, which were almost completely removed from the solution. The product fractions collected afterward (F2 and F3) showed a dramatic decrease in the capacity of adsorption of the column for carbohydrates, although some retention capacity was still observed for furfural, HMF, and lignin-derived species.

The retention for carbohydrates, mainly xylo-oligosaccharides but also monosaccharides, was calculated by integrating the RI signal of the GPC chromatograms of the feed and the samples taken during the experiment, whereas the retention for lignin and carbohydrate-degradation products (furfural and HMF) was calculated from the signal of the UV detector at 254 nm. Retentions for fractions F1−F3 were 20.2, 0.7, and 0.5% for carbohydrates and 64.3, 30.2, and 16.0% for lignin, in accordance with the preferential adsorption of lignin products over carbohydrates we observed earlier. The retentions were also calculated from the mass and composition of the nonvolatile products recovered by lyophilization of the fractions F1, F2, and F3. The results were close to those calculated from the GPC chromatograms, especially for carbohydrates.

Table 3. Adsorption on an AC-1 Activated Carbon Column: Composition of the Lyophilized Samples of the Product Fractions Collected during the Experiment and Retentions Calculated for Xylo-oligosaccharides and Lignin-Related Products (Xylo-oligosaccharide Solution from Reaction Batch 2)

		collected fractions		
	feed	F1 (0−2 h)	F2 (2−4 h)	F3 (4−5.5 h)
avg conc of dissolved products for the fraction (g/L)	35.2	25.2	33.6	33.9
Composition (% of the Dissolved Products in the Feed)				
glucose	1.84	1.28	1.76	1.75
xylose	3.95	2.81	3.96	3.97
arabinose	3.61	2.58	3.58	3.57
acetic acid	3.89	1.74	3.78	3.85
furfural	0.85	0.01	0.40	0.87
hydroxymethyl furfural	0.43	0.03	0.26	0.39
xylo-oligosaccharides	57.8	46.0	59.3	58.6
lignin-related products	6.85	2.90	5.55	5.95
ash	9.02	7.66	7.36	7.60
other (by difference)	11.8	6.78	9.49	9.84
Retention (% of Feed)				
calculated by integration of the GPC chromatograms (data in Figure 7)				
xylo-oligosaccharides (RI signal)		20.2	0.7	0.5
lignin-related products (UV signal)		64.3	30.2	16.0
calculated from the yield and chemical analysis of lyophilized samples				
xylo-oligosaccharides[a]		22.5	0.5	0.9
lignin-related products[b]		63.9	23.6	11.4

[a] Including monosaccharides, acetic acid, and ash. [b] Including furfural and HMF.

Vegas and co-workers have investigated several sequential treatments for the removal of extractive- and lignin-derived compounds from the aqueous solutions of crude xylo-oligosaccharides of barley residues[13] and rice husks.[14] After three sequential extraction stages with ethyl acetate, 6.2% of the carbohydrates and 38.2% of non-carbohydrates were removed from the solution in the case of rice husks, while for barley residues removal was 15.9% for carbohydrates and 32.9% for extractives- and lignin-related products. These values are close to those we obtained for fraction F2. Further processing of the ethyl acetate-extracted solutions with a strong anion-exchange resin increased the removal of non-carbohydrates to 78.2 and 54.0% for rice husks and barley residues, respectively, while carbohydrate removal was 22.2 and 20.4%. Our results from the F1 fraction indicate that treatment with activated carbon provides better results than extraction with ethyl acetate and that it may even produce a similar degree of removal of non-carbohydrate compounds to extraction combined with treatment with anion-exchange resins.

Conclusions

The treatment with activated carbon of raw xylo-oligosaccharide solutions obtained by autohydrolysis of lignocellulosics is a feasible option for the removal of extractives- and lignin-derived compounds and carbohydrate-degradation products. The selective adsorption of lignin products over carbohydrates has been observed for three commercial activated carbons at slightly acidic pHs. Selectivity toward lignin adsorption was higher when the carbon was highly microporous and had small mesopore diameters, a low volume of mesopores, a low concentration of basic surface groups to limit xylo-oligosaccharide adsorption, and acidic surface groups to favor the adsorption of the lignin-related products. Further studies into the tailoring of the surface properties of the carbons in order to improve selectivity and adsorption capacity for lignin-products, and into the regeneration of spent carbon beds, are under way.

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