Adsorption Behavior of Glucose, Xylose, and Arabinose on Five Different Cation Exchange Resins

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To separate xylose from monosaccharide mixtures, we investigated the adsorption equilibrium of glucose, xylose, and arabinose on five different resins. The single-component isotherms of these three sugars were measured at 25 °C. All equilibrium data were described with linear isotherms. The adsorption amounts and selectivities of the above monosaccharides on these five cation exchange resins were compared. The counterions and the degree of cross-linking were the important factors influencing the adsorption behavior. The Ca^{2+} loaded and 4 % cross-linked resin has the largest adsorption amounts for each monosaccharide, while the Ca^{2+} loaded and 6 % cross-linked resin has the maximum selectivity factor (about 1.318) for the species of arabinose and xylose and the Ca^{2+} loaded and 8 % cross-linked resin shows a better performance on the separation of xylose and glucose.

1. Introduction

Xylose is the raw material to produce xylitol by catalytic hydrogenation[1] or microbial conversion,[2] which is an alternative high-added-value sweetener with anticariogenic properties of great concern for both the food industry and the biomedical sector.[1] The critical step in the process of xylitol production is the purification of the xylose from the acid hydrolysate. Acid hydrolysis releases not only D-xylose but also appreciable amounts of D-glucose and L-arabinose.[3] These contaminating sugars can complicate the conversion of xylose to xylitol.[2] On the other hand, obtaining pure L-arabinose has commercial significance. L-Arabinose is one of the few L-sugars available freely in nature and a starting material for the production of L-ribose, an important precursor in the synthesis of antiviral drugs and rarely found in nature.[4] So the separation of these monosaccharides is necessary to maintain their functional properties.

Liquid chromatography is a high efficiency separation technique that could be useful in the current process for separation and purification of sugar mixtures.[5,6] The typical separation media are sulfonated cross-linked styrene divinylbenzene cation exchange resins.[7] The most applied instance is the industrial-scale chromatographic separation of glucose and fructose.[8−10] The mixture of arabinose, glucose, and xylose is not a usual one since their structures have small differences, especially arabinose and xylose, which are isomers, so the choice of a proper adsorbent is not a straightforward task.

Isotherms supply valuable information for the selection of a suitable adsorbent for a given separation problem, and the isotherm parameters are also required for the design of chromatographic separation processes. Since the separation of glucose and fructose is mature, the isotherm of glucose has been determined by static[11] and dynamic methods.[12] Schollner et al.[13] studied the adsorption equilibria of D-arabinose on X and Y Zeolites, and Yi Xie et al.[14] measured the isotherms of xylose and arabinose on Dowex and PVP resins for separating sugar mixture from biomass hydrolyzate. It should be noticed that there have not been studies published on the isotherms of xylose and arabinose on a series of resins for separating them from each other.

The objective of this work was the measurement of adsorption isotherms of monosaccharides on five resins and to evaluate the separation of the ternary mixture—arabinose, glucose, and xylose—by ion-exchange chromatography. A static method was used to obtain adsorption equilibrium data.

2. Experimental Section

2.1. Chemicals. Xylose was purchased from the Kaihua Huakang Pharma Co., Ltd. (> 98 % purity, Zhejiang, China) and arabinose from the Shanghai Haiqu Chemical Co., Ltd. (> 98 % purity, Shanghai, China). Glucose, potassium chloride, calcium chloride, and iron chloride of analytical grade were purchased from the Shanghai Guoyao Chemical Reagent Co., Ltd. (Shanghai, China). All solutions were prepared using deionized and filtered water.

2.2. Materials. Three gel-type strong-acid cation exchange resins purchased from the Hangzhou Zhengguang Chemical Co. (Zhejiang, China) were used in this work: 001*4H (4 % cross-linked), 001*6H (6 % cross-linked), and 001*8H (8 % cross-linked), all in hydrogen form. The properties of these three resins are listed in Table 1. The resins were converted to the calcium form by percolation with an excess of 1 M $CaCl_2$ solution and washed with deionized water. The resin 001*6H was also converted to a potassium form by percolation with an excess of 1 M KCl solution and iron form by percolation with an excess of 1 M $FeCl_3$ solution, then both were washed with deionized water. This ion-exchange procedure was verified by pH measurement.

2.3. Methods. A static method was used to determine the adsorption isotherms. The resin went through the pretreatment process first, then extraparticle liquid was removed by centrifugation. Precisely weighed resin samples with different monosac-

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Table 1. Characteristics of Adsorbents

	001*4Ca	001*6Ca	001*8Ca	001*6K	001*6Fe
functional group	$-(SO_3^-)Ca^{2+}$	$-(SO_3^-)Ca^{2+}$	$-(SO_3^-)Ca^{2+}$	$-(SO_3^-)K^+$	$-(SO_3^-)Fe^{3+}$
DVB (%)	4	6	8	6	6
particle size (μm)	180 to 250	180 to 250	180 to 250	180 to 250	180 to 250
water content (%)	39.07	37.95	28.28	38.57	38.43
total exchange capacity (mmol·g^{-1})	4.62	4.55	4.52	4.55	4.55

Table 2. Single-Component Adsorption Equilibrium Data of Glucose

001*4Ca		001*6Ca		001*8Ca		001*6K		001*6Fe	
c_E	q	c_E	q	c_E	q	c_E	q	c_E	q
g·L^{-1}	g·kg^{-1}	g·L^{-1}	g·kg^{-1}	g·L^{-1}	g·kg^{-1}	g·L^{-1}	g·kg^{-1}	g·L^{-1}	g·kg^{-1}
8.68	6.45	8.96	4.24	9.02	3.52	8.52	6.50	9.19	3.93
16.86	12.76	17.23	8.03	17.83	5.93	17.52	12.50	19.17	6.11
34.40	25.90	35.27	17.77	35.75	13.11	32.89	23.11	36.96	13.07
51.87	39.36	54.60	25.44	55.95	20.74	52.56	35.21	55.36	20.38
67.58	54.37	71.00	34.48	73.65	26.47	66.16	46.82	71.88	26.75
84.90	70.84	87.71	45.30	90.59	32.51	83.35	58.67	90.63	36.56

Table 3. Single-Component Adsorption Equilibrium Data of Xylose

001*4Ca		001*6Ca		001*8Ca		001*6K		001*6Fe	
c_E	q	c_E	q	c_E	q	c_E	q	c_E	q
g·L^{-1}	g·kg^{-1}	g·L^{-1}	g·kg^{-1}	g·L^{-1}	g·kg^{-1}	g·L^{-1}	g·kg^{-1}	g·L^{-1}	g·kg^{-1}
8.07	9.07	8.70	5.00	8.87	3.86	8.33	6.70	9.00	4.13
16.82	15.08	17.21	10.57	17.89	8.27	16.47	13.69	18.13	7.32
33.75	29.66	34.37	21.95	35.15	16.64	33.44	25.72	36.33	14.46
50.15	46.68	51.77	31.93	53.83	27.36	49.37	39.48	54.03	23.42
66.68	63.17	69.10	42.40	69.01	34.84	66.55	52.41	71.73	32.09
81.35	80.21	86.65	54.99	87.06	44.50	83.46	64.03	88.39	40.83

Table 4. Single-Component Adsorption Equilibrium Data of Arabinose

001*4Ca		001*6Ca		001*8Ca		001*6K		001*6Fe	
c_E	q	c_E	q	c_E	q	c_E	q	c_E	q
g·L^{-1}	g·kg^{-1}	g·L^{-1}	g·kg^{-1}	g·L^{-1}	g·kg^{-1}	g·L^{-1}	g·kg^{-1}	g·L^{-1}	g·kg^{-1}
7.94	9.68	8.30	6.55	8.42	5.40	7.72	8.29	8.55	5.07
15.82	19.70	16.41	13.89	16.80	10.96	15.98	15.65	17.63	9.27
31.62	39.08	32.81	27.48	33.94	20.35	31.38	33.35	35.21	18.46
48.48	56.72	49.66	39.46	50.53	31.02	47.97	47.50	52.65	29.30
63.90	75.66	65.72	55.33	68.18	40.40	63.19	64.57	69.37	40.66
80.36	92.86	83.99	69.00	84.71	52.50	80.99	77.80	87.51	50.25

charide solutions were added in a glass flask (25 mL). The glass flasks were hermetically sealed and put inside a tempered shaker at 160 rpm at 25 °C for about 12 h. This time was sufficient to reach the equilibrium which was proved by preliminary kinetic experiments.

The quantification of monosaccharide in the samples was carried out by HPLC. The HPLC system consisted of a Waters AccQ.Tag column (3.9 × 150 mm, 5 μm), a Waters 1525 HPLC pump, a Waters 717 plus autosampler, and a Waters 410 RI detector operated at 35 °C. The HPLC analytical column was placed into an oven to maintain the temperature at 30 °C. A 10 μL sample was fed into the system at a mobile phase flow rate of 0.8 mL·min^{-1}. The mobile phase was deionized and degassed water.

The concentration of monosaccharide adsorbed on the resin was calculated by mass balance according to the following equation

$$q = \frac{(c_0 - c_E)V}{m} \quad (1)$$

where q is the concentration of monosaccharide on the adsorbed phase, expressed as the amount of monosaccharide per unit amount of resin (dry basis); c_0 and c_E are the initial and equilibrium concentrations of solute in the liquid phase; V is the volume of the bulk liquid phase; and m is the mass of dry adsorbent. The dry substance content of the resin was determined by drying until constant weight in a vacuum drying oven (Jinghong, Shanghai, China) at the temperature of 80 °C.

2.4. Experimental Uncertainties. The uncertainty of the analytical balance used for weighing the amounts of monosaccharides in the sugar solution and resins was less than 0.1 %. The volume of the sugar solution was measured with an uncertainty of less than 0.5 % in all of the cases. So the uncertainty in the determination of the initial monosaccharide concentration was less than 0.51 %. The uncertainty of HPLC analysis was 0.32 %, and the dilution of the high concentration solution to the concentration in the range of standard curve has an uncertainty of less than 0.58 %. These two factors made the uncertainty in the estimation of the equilibrium concentration about 0.67 %. From eq 1, the deviations for calculated values of q were estimated to be within 0.98 %. The temperature was controlled during each experiment to be within 0.1 °C.

3. Results and Discussion

Tables 2 to 4 show the single-component adsorption data of xylose, glucose, and arabinose on five ion-exchange resins at 25 °C, respectively. The feed concentrations of each sugar were

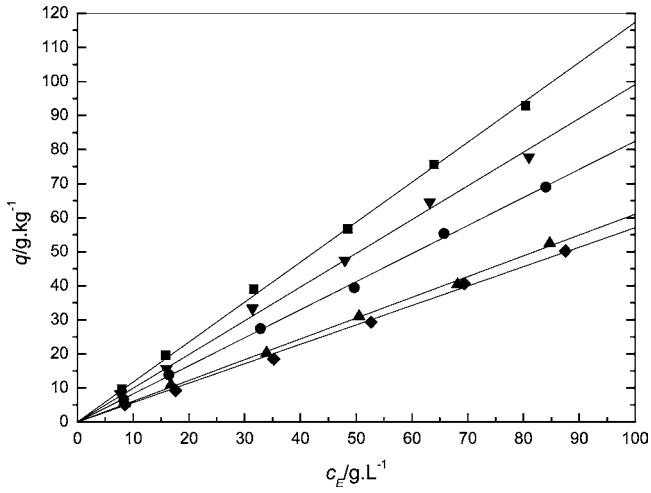

Figure 1. Single-component adsorption isotherms of arabinose on different resins. ■, 001*4Ca; ●, 001*6Ca; ▲, 001*8Ca; ▼, 001*6K; ◆, 001*6Fe. Symbols represent experimental data; lines represent best fits of eq 2.

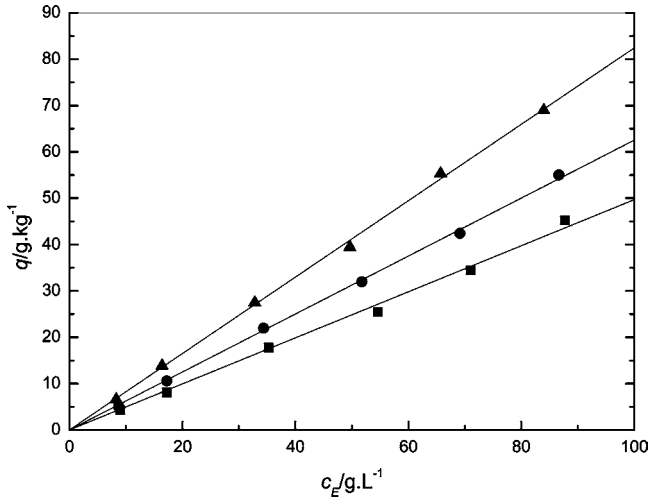

Figure 2. Single-component adsorption isotherms of xylose, glucose, and arabinose on the resin of 001*6Ca. ▲, arabinose; ●, xylose; ■, glucose. Symbols represent experimental data; lines represent best fits of eq 2.

approximately (10, 20, 40, 60, 80, and 100) g·L^{-1}. Figures 1 and 2 present the adsorption isotherms of monosaccharides on the five ion-exchange resins. Under the experimental conditions used, arabinose, glucose, and xylose are linearly adsorbed on ion exchangers. All experimental data were fitted with linear isotherms having the single parameter, the distribution coefficient K

$$q = Kc \tag{2}$$

The distribution coefficients K are presented in Table 5. One can see in Table 5 that the distribution coefficient values are all very low, and only that for arabinose on the resin of 001*4 (Ca) is larger than 1. This means the affinity between all three sugars and the stationary phase is weak. To evaluate the separation efficiency of the investigated resins, we introduce the selectivity factor (α), which has been determined by the following equation[15] and is also presented in Table 5

$$\alpha_{ij} = \frac{q_i/c_i}{q_j/c_j} = \frac{K_i}{K_j} \tag{3}$$

For the same resin, such as 001*6Ca, as shown in Figure 1, one can see that the capacity of the adsorbents with respect to individual monosaccharides decreased in the order of arabinose > xylose > glucose. This can be explained by the mechanism: ligand exchange and size exclusion. Glucose is hexose, while xylose and arabinose are pentoses. The molecular size of glucose is larger than the others. The pores in the resin exclude larger molecules. Arabinose and xylose are isomers, but arabinose has two axial−equatorial pairs of adjacent OH groups, which is more favorable for cation complex formation leading to a higher complex stability.[16] As for the selectivity factors, although all are close to 1, it can also be seen that for the resins of 001*4Ca, 001*6Ca, 001*6K, and 001*6Fe the selectivity factor for xylose/arabinose is larger than that for xylose/glucose. This means for all these four resins a better separation effect of xylose and arabinose can be achieved compared with that of xylose and glucose. The resin of 001*8Ca has the opposite tendency.

The influence of the counterions fixed on the resin constitutes one of the major parameters of the separation process. It is best demonstrated as the differences of the distribution coefficients and selectivity factors in Table 5. For the same degree of cross-linking, the K form ion-exchange resin has a higher adsorption capacity than those of the Ca form and Fe form. The interaction between sugar and cation is controlled by the modification of the hydration of the molecules.[17] K^+ binds water molecules weaker than Ca^{2+}, and Ca^{2+} binds water weaker than Fe^{3+}. Weakly bonded water is available for hydrogen bond formation with sugar molecules,[18] so the adsorbance of monosaccharide in the resins varied in the order of $K^+ > Ca^{2+} > Fe^{3+}$. However, the selectivity factors for xylose/arabinose and xylose/glucose of the Ca-form resin are the maximum. The Ca^{2+} cation has an octahedral structure and the optimum size with respect to the complexing site.[16] These two factors influence complex formation, though the complex is weak. This makes Ca^{2+} the most suitable cation for the separation of the three sugars.

Another important factor influencing the efficiency of a separation process is the degree of cross-linking of the polymer matrix expressed as a weight percentage of divinylbenzene (DVB). From Table 5, one can see that the distribution coefficients of each sugar decrease as the degree of cross-linking increases. Since a lower degree of cross-linking means a more open pore structure[19] and a higher total exchange capacity, as shown in Table 1, the 4 % DVB resin can adsorb more sugars than other resins. As for the selectivities, the 8 % DVB resin shows a better performance on the separation of xylose and glucose, while the 6 % DVB resin has the maximum selectivity factor for the species of arabinose and xylose.

Table 5. Values of the Distribution Coefficient (K) and the Selectivity Factor (α) for Different Resins[a]

		K/L·kg^{-1}			α	
resin	cation	ara	xyl	glu	ara/xyl	xyl/glu
001*4	Ca	1.174 ± 0.011	0.956 ± 0.015	0.805 ± 0.014	1.228	1.188
001*6	Ca	0.824 ± 0.007	0.625 ± 0.005	0.497 ± 0.009	1.318	1.257
001*8	Ca	0.610 ± 0.006	0.505 ± 0.005	0.361 ± 0.003	1.208	1.399
001*6	K	0.991 ± 0.015	0.779 ± 0.006	0.699 ± 0.006	1.272	1.114
001*6	Fe	0.570 ± 0.008	0.447 ± 0.008	0.383 ± 0.009	1.275	1.167

[a] ara = arabinose; xyl = xylose; glu = glucose.

4. Conclusions

Five sulfonated cross-linked styrene divinylbenzene cation exchange resins with different cross-linking (DVB) and with different counterions fixed in sulfonic groups, K^+, Ca^{2+}, and Fe^{3+}, were investigated for the separation of a mixture containing xylose, glucose, and arabinose by measuring the adsorption isotherms of three monosaccharides using a static method. The results verified that the counterions and the degree of cross-linking were the important factors influencing the adsorption behavior. The Ca form was clearly more suitable for the separation of the three sugars than the K form and the Fe form due to the higher selectivities. The 6 % DVB was more suitable for the separation of arabinose and xylose, while the 8 % DVB resin showed a better performance on the separation of xylose and glucose.

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