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Modelling of fixed-bed adsorption of mono-, di-, and fructooligosaccharides on a cation-exchange resin

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ABSTRACT

Kinetics of fixed-bed adsorption of simple saccharides (glucose, fructose, and sucrose) and fructooligosaccharides (1-kestose, 1-nystose, and 1^F-fructofuranosyl nystose) on process-size particles of cation exchanger Amberlite™ CR1320Ca was investigated. A step-up method of frontal chromatography was used when several inlet concentration steps were made in the range of 0–20 g dm^{-3}. The obtained experimental data were fitted simultaneously using the general rate model with two estimated parameters, which were the distribution coefficient of linear adsorption isotherm and solid-phase diffusion coefficient. The contribution of individual transport phenomena to dispersion of adsorption fronts was discussed.

1. Introduction

Fructooligosaccharides (FOSs), such as 1-kestose, 1-nystose and 1^F-fructofuranosyl nystose, are low-caloric, non-cariogenic, non-mutagenic compounds [1,2], whose intake is getting significant for their positive effect on human health. They stimulate adsorption of magnesium and calcium, and decrease the total cholesterol, phospholipids and triglycerides in serum [3]. Beside food such as banana, artichokes, shallot, or wheat, an important way of obtaining fructooligosaccharides is enzymatic transformation of sucrose by fructosyltransferase. The product mixture of this biotransformation contains also glucose and fructose as by-products and unreacted sucrose.

A convenient way of separating these smaller saccharides from FOSs can be continuous chromatography using microporous cation-exchange resins based on sulphonated cross-linked styrene-divinylbenzene [4–9]. Water is here used as eluent. FOSs, which are less retained by the chromatographic bed, are recovered in the raffinate whereas the smaller saccharides are collected in the extract. Both outlet streams are severalfold diluted compared to the feed. The knowledge of equilibrium and kinetics of saccharide adsorption on the ion-exchange resins is important for the design and optimization of the separation process.

Several authors have dealt with the adsorption equilibria of saccharides on commercial and non-commercial cation-exchange resins [9–11]. They found that isotherms of fructose, glucose and sucrose were linear below the concentration of 300 g dm^{-3} but slightly convex above this threshold. Gramblička and Polakovič [12] also observed the convex character of isotherms of sucrose on four commercial Ca^{2+} and Na^+ base ion-exchangers too but the isotherms of glucose and fructose were linear up to 400 g dm^{-3}. In this study, linear adsorption isotherms were also determined here for FOSs in a commercial mixture. The obtained distribution coefficients for single saccharides were used for an approximation of selectivities of individual adsorbents. The selectivities pointed out that a Ca^{2+}-based cation exchanger, Amberlite™ CR1320Ca, could be the most suitable adsorbent for chromatographic separation of FOSs.

Quantitative characterization of fixed-bed column adsorption kinetics was most investigated for glucose/fructose mixtures [5,6]. Takahashi and Goto [13] investigated the kinetics of FOSs adsorption on analytical-size particles using elution analysis for a commercial six-component mixture. A moment method was employed to estimate the distribution coefficient, intraparticle diffusion coefficient and Peclét number for each component from its corresponding elution peak. The estimated intraparticle diffusion coefficients were of the order of magnitude 10^{-11} m^2 s^{-1}.

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Nomenclature

a	particle specific surface area (m^{-1})
c	liquid-phase concentration ($kg\,m^{-3}$)
c_0	feed concentration ($kg\,m^{-3}$)
c_p	solid-phase concentration ($kg\,m^{-3}$)
c_p^*	solid-phase surface concentration ($kg\,m^{-3}$)
d_c	column inner diameter (m)
D	diffusion coefficient ($m^2\,s^{-1}$)
D_s	solid-phase diffusion coefficient ($m^2\,s^{-1}$)
d_p	particle mean diameter (m)
D_L	axial dispersion coefficient ($m^2\,s^{-1}$)
ε	bed voidage (–)
K_c	distribution coefficient (–)
k	capacity factor
K_L	overall mass transfer coefficient ($m\,s^{-1}$)
k_h	sucrose hydrolysis rate constant (s^{-1})
k_L	liquid-phase mass transfer coefficient ($m\,s^{-1}$)
k_S	solid-phase mass transfer coefficient ($m\,s^{-1}$)
L	bed length (m)
Pe	Péclet number (–)
Re	Reynolds number (–)
Sc	Schmidt number (–)
Sh	Sherwood number (–)
r	radial coordinate (m)
r_h	rate of sucrose hydrolysis to glucose and fructose ($kg\,m^{-3}\,s^{-1}$)
t	time (s)
u	interstitial velocity ($m\,s^{-1}$)
V_C	column volume (m^3)
V_0	column hold-up volume (m^3)
z	axial coordinate (m)
ν	kinematic viscosity ($m^2\,s^{-1}$)

The objective of this work was to study the kinetics of fixed-bed single-component adsorption on true process-size particles of Amberlite™ CR1320Ca for the saccharides pertinent to FOS's separation. A staircase method of frontal chromatography was employed in the concentration range of 0–20 $g\,dm^{-3}$ and the adsorption process was described by the general rate model when the distribution coefficient and solid-phase diffusion coefficient were the fitted parameters.

2. Mathematical model

General rate (GR) chromatography model was used to describe the frontal chromatography experiments. The GR model, which consisted from the material balances of a saccharide in the liquid (Eq. (1a)) and solid (Eq. (3a)) phases, exactly accounts for all effects contributing to curve broadening, i.e. axial dispersion and liquid- and solid-phase mass transfers. The model equations characterizing the liquid phase are as follows:

$$\varepsilon\frac{\partial c}{\partial t} = -\varepsilon u\frac{\partial c}{\partial z} + \varepsilon D_L\frac{\partial^2 c}{\partial z^2} - k_L a_p(1-\varepsilon)\left(c - \frac{c_p^*}{K_c}\right) \quad (1a)$$

$$t = 0 \quad 0 \le z \le L \quad c = 0 \quad (1b)$$

$$t > 0 \quad z = 0 \quad \varepsilon u(c - c_0) = D_L\frac{\partial c}{\partial z} \quad (1c)$$

$$z = L \quad \frac{\partial c}{\partial z} = 0 \quad (1d)$$

where ε is the bed voidage, c is the liquid-phase concentration, t is the time, u is the interstitial velocity, z is the axial coordinate, D_L is the axial dispersion coefficient, k_L is the liquid-phase mass transfer coefficient, a_p is the particle specific surface, c_p^* is the solid-phase surface concentration, L is the bed length, c_0 is the feed concentration, which was stepwise changed in defined times. K_c is the distribution coefficient of the linear equilibrium isotherm:

$$c_p = K_c c \quad (2)$$

where c_p and c are the solid- and liquid-phase concentrations, respectively.

The diffusional flux in the solid-phase balance (Eqs. (3a)–(3d)) was expressed through solid-phase diffusion coefficient D_s. The solid-phase related model equations are the following:

$$\frac{\partial c_p}{\partial t} = D_s\left(\frac{\partial^2 c_p}{\partial r^2} + \frac{2}{r}\frac{\partial c_p}{\partial r}\right) \quad (3a)$$

$$t = 0 \quad 0 \le r \le R_p \quad c_p = 0 \quad (3b)$$

$$t > 0 \quad r = R_p \quad D_s\frac{\partial c_p}{\partial r} = k_L\left(c - c_p^*\right) \quad (3c)$$

$$r = 0 \quad \frac{\partial c_p}{\partial r} = 0 \quad (3d)$$

where r is the radial coordinate and R_p is the particle radius.

Since a small fraction of sucrose hydrolyzed in the fixed-bed during the experiment, the model for this component was extended by the kinetic term:

$$r_h = k_h c_p \quad (4)$$

where k_h is the rate constant and r_h is the rate of sucrose hydrolysis to glucose and fructose, which was added to the left-hand side of Eq. (3a).

3. Experimental

3.1. Adsorbent

The resin used was Amberlite™ CR1320Ca (Rohm and Haas, Paris, France), which is a highly cross-linked poly(styrene)-divinylbezene cation exchanger with the functional group $-(SO_3^-)_2Ca^{2+}$. The particle diameter and ion-exchange capacity were 320 μm and 1.63 equiv L^{-1}, respectively. The value of specific surface area, $a_p = 6/d_p$, was calculated to be 18,750 m^{-1}. The resin was washed several times with double distilled water before use and was separated on a sintered-glass filter. The water content of the resin was determined by drying wet particles at 80 °C until the constant weight was reached. The value of water fraction was 48.3% with a standard deviation of 0.7%.

3.2. Equipment

Saccharide solutions or eluent water were pumped by peristaltic pumps Gilson (Gilson, Middleton, WI) through a six-port switching valve (Knauer, Berlin, Germany) at a flow rate of about 0.7–1 $cm^3\,min^{-1}$. The column was thermostated at 60 °C by means of JetStream Plus II (Thermotechnic Products, Langenzersdorf, Austria). The column outlet solution was monitored by a refractive index (RI) detector (Knauer, Berlin, Germany) and was distributed into 0.5 ml fractions using the fraction-collector Frac–920 (GE Healthcare, NY, USA). All concentrations were determined by HPLC (Knauer, Berlin, Germany) using the column REZEX RSO-Oligosaccharide (Ag^+ form, 200 mm × 10 mm, Phenomenex, Torrance, CA). The column temperature was maintained at 40 °C by the JetStream Plus II thermostat. Redistilled water was used as the mobile phase at a flow rate of 0.3 $cm^3\,min^{-1}$. The amount injected by an autosampler (Gilson, Middleton, WI) was 10 μl and