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Choice of a tracer for external porosity measurement in ion-exchange resin beds

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Abstract

The external porosity of a gel-type resin bed was evaluated from the mean residence time of a non-adsorbing solute. In order to select a tracer that does not penetrate inside the resin, the resin porosity available to the solute was evaluated by fitting breakthrough curves with a model accounting for diffusion in particles and axial dispersion in a column. Examples are given of the applicability of the method.

1. Introduction

External porosity, ε , is involved in all calculations with column applications. However, it is given far less attention than solid-phase internal porosity and most of the time, its value is arbitrarily taken to be within the range 0.38–0.4. Although this blanket estimate is reasonable in some situations, it would fail in many instances, e.g., a bed consisting of a very polydisperse particle size population, a poorly packed system such as could be encountered in routine preparative systems or a gel bed under compressive conditions (high throughput, for example); also, shrinkage and swelling of gel type resin, which occur when the bed is submitted to large variations in concentrations, may significantly affect the external porosity of the bed.

A direct and simple way to measure ε consists in purging the column: however, care must be exercised to avoid drawing off some of the liquid

contained in the stationary phase, which could alter the result. Actually, the most reliable method consists in measuring t_0 , the mean retention time of an external tracer, and calculating ε from $\varepsilon = t_0(Q/V_0)$.

A non-adsorbing solute has to be found, of course. To evaluate if a solute penetrates or not inside the resin beads, we propose to identify the dynamic response of the column with a model accounting for adsorption. A pore diffusion model is often used to describe mass transfer in macroreticular resins [1] or molecular sieve adsorbents [2]. It will be tried here on a gel-type resin in order to evaluate the internal porosity available to a solute.

2. Model and resolution

The model accounts for column hydrodynamics, axially dispersed plug-flow characterized by the column Peclet number Pe and possible diffusion of the tracer in the resin void

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volume, characterized by an internal porosity χ and apparent diffusion coefficient in the pores D_p . Negligible external fluid film resistance is assumed.

This system can be described by the following equations:

(i) mass balance in liquid:

$$\frac{1}{Pe} \cdot \frac{\partial^2 x}{\partial z^2} = \frac{\partial x}{\partial z} + \frac{\partial x}{\partial \theta} + \chi \cdot \frac{1 - \varepsilon}{\varepsilon} \cdot \frac{\partial \bar{x}_p}{\partial \theta} \quad (1)$$

(ii) mass balance in particles:

$$\frac{\partial x_p}{\partial \theta} = R_t \left(\frac{\partial^2 x_p}{\partial \rho^2} + \frac{2}{\rho} \cdot \frac{\partial x_p}{\partial \rho} \right); \quad R_t = \frac{D_p t_0}{R^2} \quad (2)$$

(iii) mean concentration of solute in particles:

$$\frac{\partial \bar{x}_p}{\partial \theta} = 3R_t \left(\frac{\partial x_p}{\partial \rho} \right)_{\rho=1} \quad (3)$$

(iv) boundary conditions:

$$\left(\frac{\partial x_p}{\partial \rho} \right)_{\rho=0} = 0 \quad (4)$$

$$\rho = 1; \quad x_p(\rho, z, \theta) = x(z, \theta) \quad (5)$$

The analytical resolution of this set of equations is performed in the Laplace domain according to a methodology described by Wilhelm [3]. The following column transfer function $H(s)$ is obtained:

$$H(s) = Pe \cdot \frac{\exp V}{U} \quad (6)$$

with

$$U = \frac{Pe}{2} \left\{ 1 + \sqrt{1 + \frac{4}{Pe} [s - g(s)]} \right\} \quad (7)$$

$$V = \frac{Pe}{2} \left\{ 1 - \sqrt{1 + \frac{4}{Pe} [s - g(s)]} \right\} \quad (8)$$

and

$$g(s) = -3\chi \cdot \frac{1 - \varepsilon}{\varepsilon} \cdot R_t \left(\sqrt{\frac{s}{R_t}} \coth \sqrt{\frac{s}{R_t}} - 1 \right) \quad (9)$$

where $g(s)$ is the transfer function characteristic of the intraparticle transport. It should be noted that the mathematical expression reached

in this way is slightly different from that given by Costa and Rodrigues [4], which included a series term.

The time domain solution of the model (pulse response) for a set of parameters χ , D_p , Pe is obtained by numerical inversion of the transfer function $H(s)$ with a fast Fourier transform algorithm. Numerical integration of the pulse response is then performed, allowing the model breakthrough curve to be obtained. Identification of the parameters and especially χ is performed by fitting the theoretical solution to the experimental breakthrough curve of a solute with the Rosenbrock optimization method [5] (square differences sum as optimized function).

As shown in Fig. 1, the model pulse response is very sensitive to χ , at least above 0.01; below this value, the pulse response seems to merge with the residence time distribution of a non-retained solute. In order to define more precisely the specification of a non-adsorbing tracer, it is interesting to evaluate the influence of χ on the precision of the external porosity determination.

The external porosity ε is obtained from the mean residence time t_0 of a non-retained solute by the well known equation

$$\varepsilon = t_0 \cdot \frac{Q}{V_b}$$

If any solute is used as a tracer, an "apparent" external porosity ε_a should be defined in place of ε :

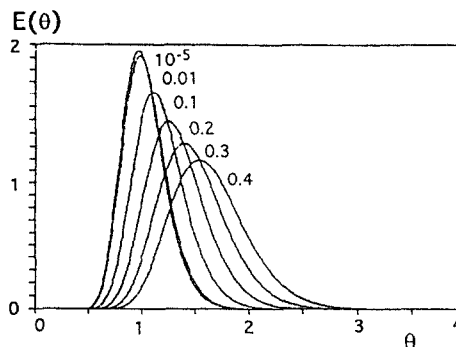


Fig. 1. Model pulse response showing the effect of varying internal porosity χ ($Pe = 50$, $R_t = 5$).

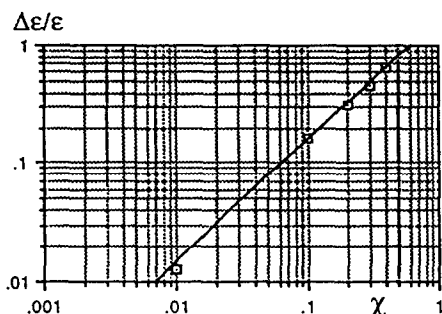


Fig. 2. Influence of χ on the relative error on external porosity measurement. Determination coefficient: $r^2 = 0.999$.

$$\varepsilon_a = \bar{t} \cdot \frac{Q}{V_b} \quad (10)$$

Then

$$\frac{\varepsilon_a - \varepsilon}{\varepsilon} = \frac{\bar{t}}{t_0} - 1 = \bar{\theta} - 1 \quad (11)$$

Hence $\bar{\theta} - 1$ measures the relative error $\Delta\varepsilon/\varepsilon$.

The parameter $\bar{\theta}$ is readily calculated from model pulse responses for several values of χ . A linear relationship is obtained when $\bar{\theta} - 1$ is plotted versus χ in a logarithmic diagram (Fig. 2). A precision of better than 1% on external porosity is obtained when the solute has a χ value lower than $7 \cdot 10^{-3}$.

3. Application of the method

3.1. Systems under investigation

In order to validate the method and test its efficiency, we give two examples of its application to the choice of an external tracer for porosity measurement on a gel-type sulfonated polystyrene resin in the Ca^{2+} form; this resin is commonly used in our laboratory to perform the separation of glucose and fructose mixtures. Two possible tracers for external fluid phase were selected: (i) a calcium salt, at relatively low concentration in order to take advantage of Donnan ion exclusion; calcium chloride was chosen; (ii) a dye whose high molecular mass

prevents it from penetrating into the resin beads; Blue Dextran was chosen.

If we may reasonably expect Blue Dextran to be a good candidate for an external tracer, it is a more tenuous prediction for calcium chloride: because of the sensitivity of the analytical measurements, concentration should be sufficiently high; however, ion exclusion decreases with increasing concentration.

3.2. Experimental

The laboratory-scale column used was obtained from Pignat (France). It was a jacketed column, 50 cm \times 5.3 cm² section, with a piston allowing feeding of solutions exactly at the top of the resin bed through a PTFE frit. Feed solution was pumped from a thermostated bath (Gilson Minipuls peristaltic pump) to the top of the bed through the piston. Electric valves ensured flexibility of use of the apparatus. A purge line was used to obtain a perfect and non-delayed step signal at the entrance of the bed. A Gilson Model 201 fraction collector was connected to the exit of the bed.

Calcium chloride was of Rectapur grade from Prolabo. Blue Dextran was for laboratory use from Sigma (M_r 2 000 000). Calcium chloride concentration was measured by conductimetry (Tacussel). Blue Dextran solutions were analysed with a Carl Zeiss PMQII spectrophotometer at a wavelength of 635 nm. Duolite C204F/2115 resin with a mean bead diameter of 471 μm was supplied by Rohm and Haas.

3.3. Results and discussion

Fig. 3 shows the breakthrough curves of CaCl_2 and Blue Dextran at 10 ml/min. Obviously, CaCl_2 is more retained than Blue Dextran and therefore cannot be considered as a good external tracer, at least at concentrations compatible with our detection means; modelling was undertaken to confirm this and to conclude that Blue Dextran was superior. All curves are well fitted by the model, as shown in Fig. 4, and allow internal porosities to be obtained (see Table 1). The very low particle internal porosity available

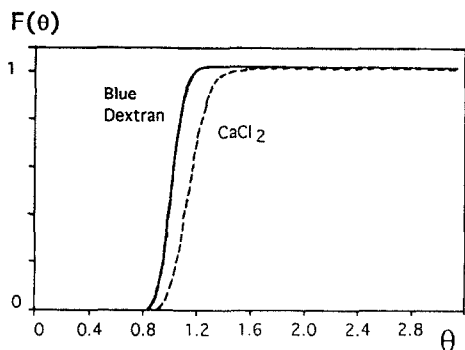


Fig. 3. Comparison of experimental breakthrough curves of CaCl_2 (dashed line) and Blue Dextran (solid line).

for Blue Dextran confirms that this solute does not penetrate into the resin and may be considered as a good tracer for an external liquid phase. In contrast, the value reached for calcium chloride, significantly higher than $7 \cdot 10^{-3}$, makes it inappropriate for this purpose. Fig. 2 indicates

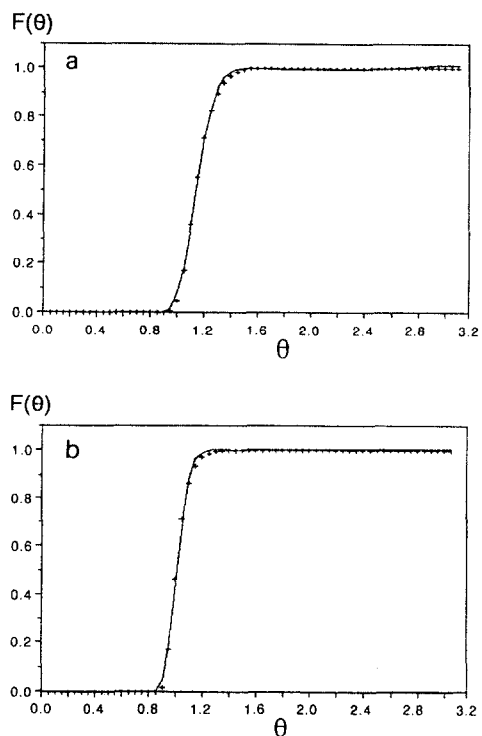


Fig. 4. Adjustment of the model (+) with experimental breakthrough curves: (a) CaCl_2 ; (b) Blue Dextran.

Table 1
Internal porosities obtained from identification of tracer breakthrough curves with the model (several runs performed for each tracer)

Run No.	χ	
	Calcium chloride	Blue Dextran
1	0.08	$0.44 \cdot 10^{-7}$
2	0.07	$0.62 \cdot 10^{-5}$
3	0.09	10^{-8}
4		$0.19 \cdot 10^{-4}$

that an error of more than 10% would be expected.

Blue Dextran breakthrough curves were recorded at different flow-rates ranging from 10 to 33 ml/min for the same bed volume, $V_b = 239 \pm 2$ ml, in order to evaluate ε . The value of t_0 can be determined either from the mass balance over the breakthrough curves or from identification with a J mixing cells in series model (parameters t_0 and $J = Pe/2$). Both methods were applied here. As shown in Fig. 5, the results obtained by either of the two methods are fully consistent and the plot of t_0 versus $1/Q$ is linear. The external porosity ε can be calculated from the slope, given the bed volume. The value obtained is $\varepsilon = 0.41 \pm 0.01$, which is in good agreement

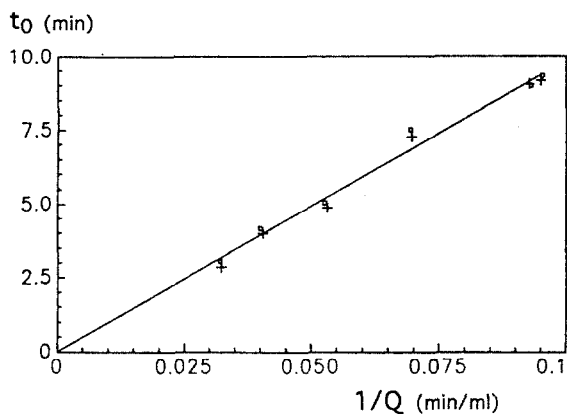


Fig. 5. Residence time t_0 plotted against $1/Q$. \square = Values obtained from mass balance over breakthrough curves; $+$ = values obtained from identification with a mixing cells in series model. Determination coefficient: $r^2 = 0.985$.

with general knowledge about the porosity of random packing of spheres.

4. Conclusions

A model accounting for axial dispersion in the external fluid phase and diffusion in the void volume of particles has been demonstrated to be efficient for selecting an appropriate tracer for an external liquid phase in a fixed bed of a gel-type ion-exchange resin. The external porosity could then be easily and accurately calculated by plotting the mean residence time against the reciprocal of flow-rate.

Symbols

D_a	axial dispersion coefficient
D_p	apparent diffusion coefficient in the pores
$E(\theta)$	column pulse response
$F(\theta)$	column step response
$H(s)$	column transfer function
L	column length
Pe	column Peclet number = uL/D_a
Q	flow-rate
R	particle radius
r	radial coordinate in particle
s	Laplace variable
t_0	mean residence time of a non-retained solute = L/u

t	time
\bar{t}	mean retention time
u	interstitial velocity
V_b	bed volume
$\frac{x_p}{x}$	concentration in particle pores
\bar{x}_p	mean concentration in particle
x	concentration in liquid phase
z	dimensionless abscissa in column

Greek letters

ε	external porosity
ε_a	apparent external porosity
ρ	dimensionless radial coordinate in particle = r/R
θ	dimensionless time = t/t_0
χ	particle porosity

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