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Correction procedures for extra-column effects in dynamic column breakthrough experiments

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Abstract

Dynamic column breakthrough experiments, routinely used to complement adsorption and diffusion studies at the particle scale, constitute an important step in the development and verification of dynamic models for simulation of adsorption processes. Various parts of the experimental set-up contribute to the retention time and band broadening of the experimental breakthrough curve. However, the effect of the extra-column contributions have to be properly accounted for in order to compare the experimental results with theoretical calculations. A common practice is to measure a blank response under the same flow rate, pressure and temperature conditions as the actual experiment by simply bypassing the adsorption column with a tube (or a connector) of negligible volume. This blank response is then subtracted point-by-point from the composite response (i.e., including the adsorption column) to account for extra-column contributions. The underlying assumption here is that blank and column responses are linearly additive, both in terms of mean residence time and band broadening. It is shown that this method of correction can, under certain operating conditions, lead to erroneous results. An alternative procedure based on linear regression is introduced and the improvements achieved by this method are illustrated using simulation examples.

Key words: Adsorption, Separation, Mathematical modeling, Parameter identification.

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28 1 Introduction

29 Gas adsorption is an extensively used industrial separation process (Ruthven,
30 1984; Yang, 1987; Ruthven et al., 1994; Ruthven, 2000; Sircar, 2002). Several
31 process configurations have been developed that skillfully exploit the adsorp-
32 tion thermodynamics and/or kinetics of the components involved to effect the
33 separation. The design of these processes depend on the accuracy with which
34 the equilibrium and kinetic parameters can be measured. Several measure-
35 ment techniques, each possessing certain advantages and disadvantages, have
36 been described in the literature (Sircar, 2007). Though static experiments,
37 such as gravimetric and volumetric can be performed to yield accurate equi-
38 librium and kinetic information, experiments have to be performed at process
39 conditions; firstly to measure the performance of the column and secondly
40 to calibrate process models that can be used for scale-up. The measurement
41 of these parameters is often influenced by effects other than adsorption, that
42 have to be properly accounted for. Failure to do so can lead to inaccurate
43 estimation of equilibrium and kinetic parameters.

44 Dynamic column breakthrough (DCB) measurement is one of the commonly
45 used experimental techniques and is a necessary step towards process devel-
46 opment as it provides information about the macroscopic performance of the
47 adsorption column. A typical DCB experiment consists of saturating the ad-
48 sorption column with a gas (or gas mixture) of a known composition and
49 switching the inlet to a gas stream that is different from the one used to
50 saturate the column. The exit gas phase composition and flow rate is mea-
51 sured with suitable detectors. From this information, equilibrium and kinetic
52 parameters can be calculated either by using analytical expressions or by fit-
53 ting the experimental results to an appropriate model. It is worth noting that
54 the “extra-column effects” or “blank contributions” arising from mechanical
55 fittings, e.g. connecting tubing, detectors and sensors influence both the resi-
56 dence time and the band broadening of the breakthrough curve. Extra-column
57 effects can be significant especially when the dead-volume in the system is not
58 negligible. This can arise either when very short columns are used (e.g. those
59 used for testing adsorbent materials available in small quantities) or when the
60 residence time in the extra-column volume is non-negligible compared to the
61 residence time in the adsorption column (Gritti et al., 2006). It is important to
62 correct the experimentally measured breakthrough curves to eliminate these
63 extra-column effects.

64 The importance of these extra-column corrections for linear chromatography
65 has been discussed in the literature (Shankar & Lenhoff, 1991; Gritti et al.,
66 2006). However, there has not been many investigations concerning adsorp-
67 tion/chromatography at non-linear conditions or when the variances of the
68 column and the extra-column responses are not additive. Traditionally, the

correction for the extra-column effects is performed by conducting experiments where the column is replaced by a zero-dead-volume blank and subtracting this response from the composite breakthrough curve. This paper highlights the shortcomings of this correction method and proposes a model based correction procedure. Using numerical simulations to describe adsorption column dynamics, the performance of the two procedures is compared and it is shown that the new procedure accounts for the extra-column contributions with higher accuracy.

2 Modeling of adsorption column dynamics

In order to study the effect of the extra-column effects, a theoretical model is used to simulate the adsorption column. The equations used for the simulation are described below:

Mass balance for adsorbable component in gas phase:

$$\frac{\partial \bar{C}}{\partial \theta} = \frac{1}{Pe} \frac{\partial^2 \bar{C}}{\partial \chi^2} - \frac{\partial \bar{v} \bar{C}}{\partial \chi} - \psi \left(\bar{C} \frac{C_{\text{in}}}{C_{\text{T}}} - 1 \right) \frac{\partial \bar{q}}{\partial \theta} \quad (1)$$

Overall mass balance for gas phase:

$$\frac{\partial \bar{v}}{\partial \chi} = -\psi \left(\frac{C_{\text{in}}}{C_{\text{T}}} \right) \frac{\partial \bar{q}}{\partial \theta} \quad (2)$$

Mass balance for solid phase:

$$\frac{\partial \bar{q}}{\partial \theta} = \gamma (\bar{q}^* - \bar{q}) \quad (3)$$

Langmuir adsorption isotherm:

$$\bar{q}^* = \frac{\bar{C}}{1 - \lambda (1 - \bar{C})} \quad (4)$$

Nondimensionalising scheme:

$$\bar{C} = \frac{C}{C_{\text{in}}}; \quad \bar{q} = \frac{q}{q_{\text{in}}^*}; \quad \chi = \frac{z}{L}; \quad \bar{v} = \frac{v}{v_{\text{in}}}; \quad \theta = \frac{t}{L/v_{\text{in}}}; \quad C_{\text{T}} = \frac{P}{R_{\text{g}} T_{\text{in}}};$$

$$\psi = \frac{q_{\text{in}}^*}{C_{\text{in}}} \frac{1 - \epsilon}{\epsilon}; \quad \gamma = \frac{kL}{v_{\text{in}}}; \quad \lambda = \frac{q_{\text{in}}^*}{q_s}; \quad q_{\text{in}}^* = \frac{KC_{\text{in}}}{1 + bC_{\text{in}}}; \quad b = \frac{K}{q_s}; \quad Pe = \frac{v_{\text{in}}L}{D_L}$$

86 An axially dispersed plug flow model is used to describe the mass balance of the
 87 adsorbable component. The overall mass balance accounts for axial variation
 88 of the velocity and a linear driving force (LDF) model is used to describe
 89 the solid phase mass balance. A Langmuir isotherm is used to represent the
 90 adsorption equilibrium. In the present study, the gas phase is considered to
 91 have two components: an adsorbable component and an inert carrier. The
 92 equations were discretized in space using orthogonal collocation and integrated
 93 in time using FORSIM - a stiff ordinary differential equation solver developed
 94 in Fortran (A.E. Canada, 1976).

95 3 Point-by-point correction

96 A simplified schematic of a DCB experimental set-up is shown in Fig. 1 (a). In
 97 brief, the system consists of gas tanks, a multi-position switch valve, a mass
 98 flow controller, an adsorption column, a mass flow meter, a back pressure reg-
 99 ulator and a detector. For measuring the adsorption breakthrough curve, the
 100 column is initially saturated with an inert gas that flows through the column.
 101 At time $t = 0$, the gas flow is switched from the inert to an adsorbate of
 102 known composition. For measuring the desorption breakthrough, the proce-
 103 dure is reversed, i.e., the column is initially saturated with an adsorbate of
 104 known concentration and at time $t = 0$, the gas flow is switched to an inert.
 105 In both cases, the gas flow rate is controlled upstream of the column using a
 106 mass flow controller while the exit flow rate and concentration are measured
 107 using suitable detectors. It is worth noting that the sorption process can sig-
 108 nificantly affect the downstream volumetric flow rate and has to be properly
 109 accounted for to obtain reliable information (Malek et al., 1995).

110 Traditionally, a “point-by-point” (PBP) procedure is used to eliminate the
 111 extra-column effects and obtain the *true response* of the adsorption column (Fa-
 112 rooq et al., 2002; Guntuka, 2006). Two sets of experiments are usually per-
 113 formed whose simplified schematics are shown in Fig. 1. The first experiment
 114 consists of measuring the *composite response* which represents the cumula-
 115 tive contribution of the extra-column volumes and the column. In the second
 116 experiment, the column is replaced by a zero-dead-volume connector whose
 117 contribution to residence time and band broadening is considered negligible
 118 and the experiment is repeated at the same inlet flow rate as the first experi-
 119 ment. This response termed *blank response* is shown along with the composite
 120 response in Fig. 2. In order to obtain the corrected response corresponding

breakthrough times for a particular gas phase concentration is considered: t_C being that of the composite response and t_B being that of the blank response. The corrected breakthrough time, t_{correc} is then calculated as:

$$t_{\text{correc}} = t_C - t_B \quad (5)$$

By performing this calculation over the entire concentration scale, the corrected breakthrough profile, as shown in Fig. 2 is obtained. This profile is *expected* to be the true response of the adsorption column to an ideal step input. The correction hinges on the assumption that the retention time and the band broadening are linearly additive and the adsorption breakthrough and the blank experiments are essentially performed at identical conditions.

4 Modeling dispersion in extra-column volume: Tanks-in-series model

The mixing in tubings and fittings, can be described in different ways with the two popular alternatives being: 1. Tanks-in-series and 2. Axial dispersion models (Levenspiel, 1998). Both are single parameter models, with the number of tanks, N , and the axial dispersion coefficient, D_L being the characteristic parameters for the two cases, respectively. The two extremes of mixing, namely plug flow and complete mixing can be described by these models through appropriate choice of these characteristic parameters.

In this work, the tanks-in-series (TIS) model is considered whose schematic is shown in Fig. 3(a). It is assumed that the lumped contribution of the tubing, detector and other fittings can be described by a system consisting of N equi-volume well mixed tanks connected in series. In essence, the response of the breakthrough apparatus can be modeled as shown in Fig. 3(b) with no distinction being made between mixing in the tubing, the detector and other fittings.

In the TIS model, the mass balance around the tank k can be represented by

$$\frac{dC_k}{dt} = \frac{Q(t)}{V_{\text{dead}}/N} (C_{k-1}(t) - C_k(t)) = \frac{1}{\tau(t)} (C_{k-1}(t) - C_k(t)); \quad k = 1, 2, \dots, N \quad (6)$$

where V_{dead} is the total dead volume, i.e. the sum of the volumes of fittings, connecting tubing, detector, etc. and τ is the residence time in a tank. The flow rate $Q(t)$ is considered to be varying with time. The above equation has two unknown parameters, the dead volume, V_{dead} and the number of tanks,

150 N . The dead volume, V_{dead} can either be independently measured (e.g. by
 151 filling the tubing with a suitable liquid and measuring the volume), or can be
 152 experimentally determined (e.g. by measuring the residence time of a dilute
 153 pulse). The number of tanks, N is fitted to the experimental results to match
 154 the breakthrough profile. Note that $C_N(t)$, i.e. the outlet concentration of the
 155 N th tank corresponds to the measured composite response $C_{\text{out}}(t)$.

156 In order to validate the model and to demonstrate that it can be used to
 157 describe mixing in standard breakthrough apparatus, experiments were per-
 158 formed using a commercial oxygen detector [Model no: Servomex 572; Ser-
 159 vomex Limited, Sussex, England]. The details of the experimental set-up are
 160 given elsewhere (Guntuka, 2006; Guntuka et al., 2007). The experiments were
 161 conducted at flow rates lower than the recommended range in order to clearly
 162 demonstrate the contribution of the dead volume to the residence time and
 163 the band broadening. In this set-up, the detector was connected directly to
 164 the downstream of the mass flow controller. The system was flushed with ni-
 165 trogen and at time $t = 0$, the flow was switched to oxygen. Experiments were
 166 conducted at two different volumetric flow rates namely 37.6 mL/min and 106
 167 mL/min. The measured responses are shown in Fig. 4. Using the TIS model
 168 described above, both V_{dead} and N were fitted to the experimental profiles
 169 by reducing the sum of the errors between the experimental and calculated
 170 responses. The best fit was obtained for $V_{\text{dead}} = 64$ mL and $N = 11$. The
 171 corresponding calculated responses are also shown in Fig. 4. It can be seen
 172 that barring a minor mismatch in the latter part of the breakthrough curve
 173 corresponding to 106 mL/min, the fit is good. Hence, from this example, it
 174 can be argued that the TIS model offers good representation of mixing in the
 175 detector and that N can indeed be considered invariable within the range of
 176 flow rates considered (note that the two flow rates used vary by a factor of
 177 2.8).

178 5 Inversion of tanks-in-series model

179 In the previous section, we demonstrated that the TIS model can indeed be
 180 used for the description of the dispersion in the detector. In this section, we
 181 use the TIS model for handling corrections for “extra-column” effects, i.e.
 182 estimation of the true response of the column, $C_0(t)$ from the experimentally
 183 measured composite response, $C_{\text{out}}(t)$. We first note that a rearrangement of
 184 Eqn. 6 gives

$$C_{k-1}(t) = C_k(t) + \tau(t) \frac{dC_k}{dt} \quad k = 1, 2, \dots, N \quad (7)$$

185 The above expression suggests that $C_{N-1}(t)$ can be calculated based on the
 186 measured response $C_N(t)$ by using a finite difference approximation of the
 187 derivative term. By continuing this procedure, it may seem possible to com-
 188 pute $C_0(t)$ using Eqn. 7. A practical difficulty in using this approach is that the
 189 derivative term amplifies the measurement noise present in $C_N(t)$ and hence
 190 the calculated $C_0(t)$ becomes non-smooth. Furthermore, the use of finite dif-
 191 ference approximation inherently introduces some error in the estimation of
 192 $C_{k-1}(t)$ from $C_k(t)$. Numerical examples show that even when measurement
 193 noise is not present, the error manifests itself as oscillations in the computed
 194 profiles of $C_0(t)$, especially for large N . The presence of oscillations in the
 195 computed $C_0(t)$ can also be attributed to the non-causality, i.e. the estima-
 196 tion of cause from effect, of the model in Eqn. 7. These difficulties necessitates
 197 the use of regression based techniques to estimate $C_0(t)$ from measured $C_N(t)$,
 198 as discussed in the rest of the section. We first deal with the case of constant
 199 volumetric flow rate at the exit of the column Q_0 (e.g. when the adsorbable
 200 component is in trace quantities) followed by the case of time-varying $Q_0(t)$.

201 5.1 Constant volumetric flow rate

202 As the composite response, $C_{\text{out}}(t)$ is only measured at finite number of time
 203 instances, we need a discretized version of the TIS model in Eqn. 6 for re-
 204 gression purposes. Such a discretized model can be obtained using forward
 205 or backward difference to approximate the derivative term in Eqn. 6. In this
 206 paper, we instead use Laplace transform followed by discretization using zero-
 207 order hold to get a more accurate discretized model. Specifically, the latter
 208 method ensures the response of $C_{\text{out}}(t)$ from the discretized model and dif-
 209 ferential equation model given by Eqn. 6 are the same for a step change in
 210 $C_0(t)$.

211 Now, denoting the deviation variables as $\hat{C}_k(t) = C_k(t) - C_k(0)$ and using
 212 Laplace transform, the TIS model can be expressed in the transfer function
 213 form as (Seborg et al., 2003)

$$\begin{aligned}
 \frac{\hat{C}_k(s)}{\hat{C}_{k-1}(s)} &= \frac{1}{\tau s + 1}; \quad k = 1, 2, \dots, N \\
 \Rightarrow \frac{\hat{C}_N(s)}{\hat{C}_0(s)} &= \prod_{k=1}^N \frac{\hat{C}_k(s)}{\hat{C}_{k-1}(s)} = \frac{1}{(\tau s + 1)^N}
 \end{aligned} \tag{8}$$

214 Based on Eqn. 8, we note that the estimation of the inlet concentration profile
 215 $C_0(t)$ through direct inversion of the TIS model is not possible as the inverse of
 216 the model between $\hat{C}_0(s)$ and $\hat{C}_N(s)$ is non-causal and a method for overcoming
 217 this difficulty is discussed next.

218 To obtain a discretized model, let Δt represent the difference between the suc-
 219 cessive time instants at which outlet concentration is recorded. For simplicity,
 220 we assume that Δt does not change during the experiment. In practice, this
 221 assumption can be satisfied in two ways: 1.) By performing data acquisition
 222 at desired time intervals or 2.) by using (nearest neighbor or spline) interpo-
 223 lation on the irregularly recorded outlet concentration profile. The transfer
 224 function model between $\hat{C}_0(s)$ and $\hat{C}_N(s)$ is discretized using zero-order hold
 225 with a sampling period Δt and g_j is taken as the j^{th} step response coeffi-
 226 cient of the discretized model. Then, the outlet concentration profile $\hat{C}_N(i)$,
 227 $i = 1, 2, \dots, n_{\text{samp}}$ can be computed using convolution as (Seborg et al., 2003)

$$\hat{C}_N(i) = \sum_{j=1}^i g_j \Delta \hat{C}_0(i-j+1); \quad i = 1, 2, \dots, n_{\text{samp}} \quad (9)$$

228 where $\Delta \hat{C}_0(i-j+1) = \hat{C}_0(i-j+1) - \hat{C}_0(i-j)$ with $\Delta \hat{C}_0(1) = 0$. For
 229 notational convenience in subsequent discussion, Eqn. 9 is represented in the
 230 matrix form as

$$\hat{\mathbf{C}}_N = G \Delta \hat{\mathbf{C}}_0 \quad (10)$$

231 where

$$\begin{aligned} \hat{\mathbf{C}}_N^T &= [\hat{C}_N(1) \ \hat{C}_N(2) \ \dots \ \hat{C}_N(n_{\text{samp}})]^T \\ \Delta \hat{\mathbf{C}}_0^T &= [\Delta \hat{C}_0(1) \ \Delta \hat{C}_0(2) \ \dots \ \Delta \hat{C}_0(n_{\text{samp}})]^T \end{aligned}$$

232 and G is a Hankel matrix defined as

$$G = \begin{bmatrix} g_1 & 0 & 0 & \dots & 0 \\ g_2 & g_1 & 0 & \dots & 0 \\ g_3 & g_2 & g_1 & \dots & 0 \\ \vdots & \vdots & \ddots & \dots & \vdots \\ g_{n_{\text{samp}}} & g_{n_{\text{samp}}-1} & g_{n_{\text{samp}}-2} & \dots & g_1 \end{bmatrix}$$

233 Let $\hat{\mathbf{C}}_{N,m}$ denote a vector containing the measured outlet concentration profile
 234 expressed in terms of deviation variables, *i.e.*

$$\hat{\mathbf{C}}_{N,m}^T = [\hat{C}_{N,m}(1) \ \hat{C}_{N,m}(2) \ \dots \ \hat{C}_{N,m}(n_{\text{samp}})]^T$$

235 with $\hat{C}_{N,m}(i) = C_{N,m}(i) - C_{N,m}(0)$. Here, a robust estimate of the initial
 236 steady-state value $C_{N,m}(0)$ can be obtained by taking the average of first few
 237 experimental data points.

238 It may seem that the inlet concentration profile can be estimated by minimiz-
 239 ing the sum of squared errors (SSE), i.e. the difference between the measured
 240 and predicted outlet concentration profiles:

$$\min_{\Delta \hat{\mathbf{C}}_0} \left(\hat{\mathbf{C}}_{N,m} - G \Delta \hat{\mathbf{C}}_0 \right)^T \left(\hat{\mathbf{C}}_{N,m} - G \Delta \hat{\mathbf{C}}_0 \right) \quad (11)$$

241 As G is a square matrix, the optimal solution for the optimization problem in
 242 Eqn. 11 is given as $\hat{\mathbf{C}}_0^* = G^{-1} \hat{\mathbf{C}}_{N,m}$. However, we recall that inverse of the TIS
 243 model is non-causal. This implies that the Hankel matrix G is non-invertible
 244 and the inlet concentration profile estimated as $G^{-1} \hat{\mathbf{C}}_{N,m}$ will result in large
 245 variations.

246 These large variations in the inlet concentration profile can be avoided through
 247 regularization or Ridge regression, where the variation of inlet concentration
 248 is penalized (Tikhonov, 1963; Hoerl & Kennard, 1970). In particular, the fol-
 249 lowing optimization problem is solved

$$\min_{\Delta \hat{\mathbf{C}}_0} \left(\hat{\mathbf{C}}_{N,m} - G \Delta \hat{\mathbf{C}}_0 \right)^T \left(\hat{\mathbf{C}}_{N,m} - G \Delta \hat{\mathbf{C}}_0 \right) + \beta \left(\Delta \hat{\mathbf{C}}_0^T \Delta \hat{\mathbf{C}}_0 \right) \quad (12)$$

250 where $\left(\Delta \hat{\mathbf{C}}_0^T \Delta \hat{\mathbf{C}}_0 \right)$ is the norm of the input change. In Eqn. 12, the regular-
 251 ization or Ridge parameter $\beta > 0$ provides a trade-off between the prediction
 252 error and variation of inlet concentration profile. By finding the stationary
 253 point of the expression in Eqn. 12, the optimal solution can be derived as

$$\Delta \hat{\mathbf{C}}_0^* = (G^T G + \beta I)^{-1} G^T \hat{\mathbf{C}}_{N,m} \quad (13)$$

254 Based on Eqn. 13, the estimated inlet concentration profile is given as

$$C_0^*(i) = C_{N,m}(0) + \sum_{j=1}^i \Delta \hat{C}_0^*(j); \quad i = 1, 2, \dots, n_{\text{samp}} \quad (14)$$

255 Note that the initial value of C_0 is taken to be same as the initial value of
 256 measured outlet concentration. This is reasonable as the TIS model has unity
 257 gain (see Eqn. 8).

258 Note that as β is increased, the inlet concentration profile becomes smoother,
 259 but the prediction error increases. There are a number of methods available for

appropriate selection of β . In this paper, we use the L -curve method (Hansen, 1992), where the SSE $(\hat{\mathbf{C}}_{N,m} - G \Delta \hat{\mathbf{C}}_0^*(\beta))^T (\hat{\mathbf{C}}_{N,m} - G \Delta \hat{\mathbf{C}}_0^*(\beta))$ and inlet concentration variation $(\Delta \hat{\mathbf{C}}_0^T(\beta) \Delta \hat{\mathbf{C}}_0(\beta))$ are computed for different values of β and plotted against each other. This curve has an L shape and β is selected around the corner of this curve.

5.2 Varying volumetric flowrate

Next, we propose an approach to handle the case where the volumetric flowrate Q_0 itself changes during the experiment (e.g. bulk adsorption). We consider that the effect of change in Q_0 is instantaneously reflected across all N tanks. Denoting Q_{in} as the flowrate at the column inlet, the transfer function model between $\hat{C}_0(s)$ and $\hat{C}_N(s)$ can be derived as

$$\frac{\hat{C}_N(s)}{\hat{C}_0(s)} = \frac{1}{\left(\frac{\tau}{Q_0/Q_{\text{in}}}s + 1\right)^N} \quad (15)$$

As the measurement of Q_0 is only available at a finite number of points, we reasonably assume that Q_0 remains constant between two successive measurements. Then, the TIS description in Eqn. 15 can be seen as a piecewise linear model with a varying time constant. By discretizing the model with a sampling period of Δt and following the same procedure, as used for the case of constant volumetric flow rate in Section 5.1, it can be shown that the relationship in Eqn. 10 still holds, except that the Hankel matrix G needs to be modified as

$$G = \begin{bmatrix} g_1(1) & 0 & 0 & \cdots & 0 \\ g_2(2) & g_1(2) & 0 & \cdots & 0 \\ g_3(3) & g_2(3) & g_1(3) & \cdots & 0 \\ \vdots & \vdots & \ddots & \cdots & \vdots \\ g_{n_{\text{samp}}}(n_{\text{samp}}) & g_{n_{\text{samp}}-1}(n_{\text{samp}}) & g_{n_{\text{samp}}-2}(n_{\text{samp}}) & \cdots & g_1(n_{\text{samp}}) \end{bmatrix} \quad (16)$$

where $g_j(i)$ is the j^{th} step response coefficient of the discretized form of Eqn. 15 with $Q_0 = Q_0(i)$, $i = 1, 2, \dots, n_{\text{samp}}$. With G in Eqn. 16, the optimal estimate of inlet concentration profile can be computed using Eqn. 13 and Eqn. 14. This formulation is more general and the situation when Q_0 is a constant over time is a special case.

284 The performance of the inversion procedure was tested using simulations. As
 285 a test case, a system with $N = 20$ and $V_{\text{dead}} = 60$ mL and an inlet flow
 286 rate of 60 mL/min was considered. An arbitrary breakthrough curve, i.e. the
 287 true response of an adsorption column, was considered as an input to the TIS
 288 model and by solving Eqn. 6, $C_N(t)$ was obtained. This response, equivalent to
 289 $C_{\text{out}}(t)$, was corrected for extra-column effects using the inversion procedure
 290 described above. The effect of the parameter β on the SSE is shown in Fig. 5,
 291 where the characteristic “L” shape can be observed. As discussed, $\beta = 0.1$ - a
 292 value around the corner of the curve was chosen for the inversion.

293 Two examples, one where the volumetric flow rate is constant over the period
 294 of the experiment and the other, where the flow rate varies with time were
 295 considered. Figure 6 (a) corresponds to a situation in which the volumetric flow
 296 rate is assumed to be constant throughout the duration of the experiment and
 297 it can be seen that the performance of the inversion procedure is good since the
 298 true and the corrected responses are identical. Figure 6 (b) corresponds to a
 299 situation where the exit volumetric flow rate varies with time as shown. Using
 300 this information the inversion was performed and the results demonstrate that
 301 the true and corrected results are indeed identical.

302 6 Results and discussion

303 In the earlier sections, it has been shown that the TIS model is well suited to
 304 describe the dynamics of extra-column volumes and that the model inversion
 305 can be achieved using regression based method. In this section the shortcom-
 306 ings of the PBP correction procedure is demonstrated and it is shown that
 307 the TIS model provides better correction.

308 For the sake of simplicity a dead volume of 60 mL is considered. With respect
 309 to the number of tanks, two cases are considered: namely $N = 5$ and $N = 20$.
 310 Note that these two cases represent situations that are both less well-mixed
 311 ($N = 20$) and more well-mixed ($N = 5$) compared to the experimental system
 312 for which $N = 11$ as discussed in Section 4.

313 For each example, the following three responses to a step input are simulated:
 314 1.) Blank response ; 2.) True response; and 3.) Composite response. The blank
 315 response is simulated using the tanks in series model as represented by Eqn. 6,
 316 while the true response of the column is simulated using the equations listed
 317 in Section 2. The composite response of the system is simulated by process-
 318 ing the true response of the column through the tanks-in-series model. It is
 319 worth noting that we had demonstrated that the TIS model can indeed be
 320 used to describe extra-column in Section 4. Hence, it can be argued that this
 321 model adequately captures the contribution of the extra-column volume both

in terms of residence time and band broadening. Note that these simulations are designed to mimic the experimental runs, i.e. all three runs are performed at a pre-determined inlet flow rate and composition. Using these profiles, the two correction procedures, namely PBP and TIS are applied and the corrected response of the column to a step input is calculated. The profiles obtained by the two methods are then compared with the true response of the adsorption column. The parameters used for the various cases are given in Tables 1 and 2

6.1 Case 1

As a first example, we consider a trace system ($X_{\text{in}} = 0.05$) with a moderate non-linearity ($\lambda = 0.10$). The simulations and results for this case are shown in Fig. 7. Owing to the trace amount of the adsorbable component in the feed, the variation of the exit flow rate is negligible. The composite response was corrected for the effect of the blank using the PBP method and the results are compared with the true response of the column. Both the true and corrected responses are fairly symmetric about their mean residence time. While the corrected response estimates the mean residence time well, the estimation of the band broadening is rather poor. For both cases, i.e., $N = 5$ and $N = 20$, the PBP method estimates a sharper response than the true response of the column. This is a clear pitfall of the method and will lead to an overestimation of the mass transfer parameter if they are fitted to this response. As can be seen from the figure, the deviation of the corrected response from the true response is larger in the case of $N = 5$ as compared to $N = 20$. The TIS method with $\beta = 0.1$ was used to correct for the extra-column effects and results are plotted in Fig. 7. As can be seen from the figure, the match between the corrected and true response of the column is excellent.

6.2 Case 2

As a second example we consider a system which involves a trace system ($X_{\text{in}} = 0.05$) with a higher isotherm non-linearity ($\lambda = 0.5$). Further, the LDF coefficient is smaller as compared to Case 1. The results are shown in Fig. 8. This case corresponds to a situation where the variation of the exit flow rate over time is rather negligible as the inlet stream contains only 5 % of the adsorbable component. First we consider the corrected profiles using the PBP scheme. From the figures it can be seen that in both cases, i.e. $N = 5$ and $N = 20$ the corrected profile has a mean residence time identical to that of the true response of the column. However, the PBP method predicts a sharper response compared to the true response of the column. Further, it can be ob-

served that a sharp breakthrough at $t < 50$ s is seen in the true response. This is a signature of systems that are characterized by barrier resistance (Farooq et al., 2002)¹. However, this characteristic take-off is conspicuously absent in the corrected profile. Similar to Case 1, the PBP corrected response approaches the true response when N increases. Hence, the PBP method not only estimates a sharper response but also masks signature features of actual mass transfer resistances such as barrier resistances confined at the mouth of a microporous adsorbent. As a next step, the TIS model was used for the correction and the profile is shown in the same plot. It can be clearly seen that this procedure captures the true response of the column perfectly. It captures the mean retention time, the band broadening and the characteristic take-off well.

6.3 Case 3

The third example considers a system where the inlet flow rate is five times that of the previous cases. Further, the amount of adsorbable components in the feed is increased to 50%. The results are shown in Fig. 9. It is worth noting that owing to significant amount of the adsorbable component in the feed, the exit flow rate change in this case is non-negligible. Under these conditions, the residence time in the column is much larger compared to the residence time in the blank. Both PBP and TIS schemes produce identical results which compare well with the true response of the column. In this case, owing to the high flow rate, the detector behaves like a plug flow system and hence its contribution to the band broadening, compared to that of the column, is negligible.

6.4 Case 4

The fourth example concerns a system with a fairly non-linear isotherm, $\lambda = 0.9$ and with the inlet mole fraction being $X_{\text{in}} = 0.5$. The results are shown in Fig. 10. The high fraction of adsorbable component leads to a significant change in the flow rate as the breakthrough proceeds. The PBP correction method not only produces a sharper response, but also results in a lower average retention time as compared to the true column response. This is especially visible in the Fig. 10 (b). This arises due to the fact that while the composite response is influenced by the change in flow rate, the detector response used in the PBP correction is measured at a constant flow rate which is equal to the column inlet flow rate. This is a key shortcoming of the PBP

¹ It should be mentioned that the LDF formulation is the correct model for describing systems that show barrier resistance.

method, and could be of concern especially when bulk adsorption is involved. In such cases, the PBP procedure could not only result in an error in the mass transfer parameters, but also result in the incorrect estimation of equilibrium parameters that might be fitted to these breakthrough curves. The comparison of the TIS corrected profile with the true column response is also shown in the same figure. It can be clearly seen that this procedure captures both the retention and band broadening well. This result is not surprising as the TIS model explicitly uses the information about the exit flow rate to perform the correction and hence allows for a better correction.

6.5 Case 5

As a final example we consider an extreme case where the mass transfer coefficient is fairly small $k = 0.001\text{s}^{-1}$. The results for this case are shown in Fig. 11. The adsorbable component is diluted in the carrier and hence the variation in the exit flow rate is negligible. However, since the mass transfer coefficient is small, a very sharp breakthrough followed by a long tail is observed. The profile obtained using the PBP method is shown alongside. As in the previous cases, the PBP correction yields a sharper response compared to the true response of the column.

When the TIS correction procedure is applied, the corrected profile obtained, while being closer to the true response, yields spurious oscillations. This behaviour results as according to the TIS model, the inlet concentration profile should rise sharply similar to the true response of the column. However, in the formulation of the optimization problem in Eqn. 12, sharp changes in inlet concentration profile are penalized which gives rise to oscillations in the estimated $C_0(t)$.

While a theoretically sound method for elimination of the oscillations in the estimated inlet concentration profile is being currently researched, we present a simple heuristic based method to overcome this difficulty in the following discussion. From the previous examples, we note that during the adsorption process, $C_0(t)$ monotonically increases with time. In the presence of spurious oscillations, however, the gradient of $C_0(t)$ becomes negative at certain times. Thus, the oscillations in $C_0(t)$ can be removed by solving a constrained optimization problem with the objective function being given by Eqn. 12 and non-negativity constraints on $\Delta\hat{\mathbf{C}}_0$, i.e.

$$\Delta\hat{\mathbf{C}}_0(i) \geq 0; \quad i = 1, 2, \dots, n_{\text{samp}} \quad (17)$$

The corresponding constraint for a desorption experiment can be written as

$$\Delta\hat{\mathbf{C}}_0(i) \leq 0; \quad i = 1, 2, \dots, n_{\text{samp}} \quad (18)$$

429 The resulting optimization problem can be easily cast a quadratic program-
 430 ming problem and can be solved using available mathematical tools, e.g.
 431 *quadprog* in the optimization toolbox of Matlab. As seen from Fig. 11, the
 432 introduction of the constraints dampens the oscillation resulting in more re-
 433 alistic breakthrough profiles. However, we do recognize that this method of
 434 formulating constraints will fail for systems exhibiting “roll-up” effects owing
 435 to competitive adsorption between components involved (Santacesaria et al.,
 436 1982).

437 7 Conclusion

438 The correction of breakthrough profiles for extra-column effects was studied.
 439 Traditionally, a point-by-point correction scheme has been used which im-
 440 plicitly assumes linear additivity of the retention time and band broadening.
 441 This paper highlights the potential pitfalls of this method. It has been shown
 442 that this procedure often results in a sharper breakthrough curve as compared
 443 the true response of the column leading to incorrect estimation of the mass
 444 transfer coefficients and equilibrium parameters. In cases where the exit flow
 445 rate changes as the breakthrough proceeds, the PBP scheme also leads to dis-
 446 crepancies in retention time. In some cases, it was also shown that the PBP
 447 can provide misleading information by masking characteristic mass transfer
 448 resistances.

449 In this paper we suggest that the extra-column effects be modeled as tanks-
 450 in-series, and further propose an inversion algorithm that is able to overcome
 451 the pitfalls of the PBP method This was demonstrated using a host of ex-
 452 amples. It has been shown that the inversion of TIS model provides a more
 453 accurate method for correction of breakthrough profiles over a wider range of
 454 operating conditions as compared to the PBP scheme. An alternate approach
 455 will be to compare the composite responses from experiments and simula-
 456 tions, as opposed to comparing the true responses. This method, it might
 457 appear, can circumvent the correction of the composite response to obtain the
 458 true response. However, the importance of obtaining the true response are the
 459 following: Firstly, key information concerning underlying mass transfer mecha-
 460 nisms may be masked by the dynamics of the extra-column volume (note that
 461 in Fig. 8 the characteristic take-off, a signature of systems exhibiting bar-
 462 rier resistance, is smoothened out by the extra-column dynamics). Secondly,
 463 practitioners wishing to obtain equilibrium and kinetic parameters by fitting
 464 experimental results to analytical solutions of column dynamics equations, e.g.
 465 methods based on the calculation of moments, should base their analysis on

the true response rather than on the composite response. In conclusion, we have identified regions where the PBP correction procedure leads to incorrect prediction of the true response of the column, while the TIS model makes a more accurate prediction. However, it should be mentioned that the choice of the model to be used depends largely on the accuracy that the user intends to achieve from the experiments.

8 Software

A free copy of the Matlab code used for the inversion of the TIS model can be obtained by contacting the corresponding author.

9 Notation

b	Langmuir isotherm parameter
C	Gas phase concentration of adsorbable component
C_T	Total gas phase concentration
$\bar{C}$	Dimensionless gas phase concentration of adsorbable component
$\hat{C}$	Deviation variable for concentration
D_L	Axial dispersion coefficient
G	Hankel matrix
k	LDF coefficient
K	Henry constant
L	Length of the adsorption column
n_{samp}	Number of samples
N	Number of tanks
q	Solid phase concentration of adsorbable component
q_s	Solid phase concentration at saturation of adsorbable component
$\bar{q}$	Dimensionless solid phase concentration of adsorbable component
q^*	Equilibrium solid phase concentration of adsorbable component
P	Pressure
Pe	Peclet number
Q	Volumetric flow rate
R_g	Universal gas constant
t	Time
T	Temperature
v	Velocity
$\bar{v}$	Dimensionless velocity
V_{dead}	Dead volume
z	Axial coordinate

476 Subscripts and Superscripts

in	Conditions at column inlet
out	Conditions at exit of the last tank
0	Conditions at column exit

477 Greek symbols

β	Ridge parameter
γ	Dimensionless LDF coefficient
θ	Dimensionless time
ϵ	Void fraction of the column
χ	Dimensionless length
λ	Langmuir non-linearity parameter
τ	Tank residence time in the TIS model
ψ	Dimensionless phase ratio

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524 Press, London.

525 **List of Figure Captions**

526 Figure 1:

527 Simplified schematic for various experiments performed to correct for extra-
528 column contributions.

529 Figure 2:

530 Qualitative responses for experimental configurations shown in Fig. 1 and
531 illustration of the point by point correction procedure.

532 Figure 3:

533 Schematic of the tanks-in-series (TIS) model for description of extra-column
534 effects.

535 Figure 4:

536 Experimental (symbols) responses of direct injection into the detector. Fitted
537 volume = 64 mL, number of tanks, $N=11$. Lines depict the fitted response
538 using a tanks-in-series model.

539 Figure 5:

540 Plot of sum of squared errors as a function of the norm of input change for
541 example shown in Fig.6 (a).

542 Figure 6:

543 Inversion of the TIS model for (a) no variation of inlet flowrate and (b) with
544 variation inlet flowrate.

545 Figure 7:

546 Comparison of PBP and TIS inversion techniques corresponding to Case 1.
547 Legend: (o)- True response of the column, C_0/C_{in} ; (♦) - Composite response,
548 C_{out}/C_{in} ; (◇) - Blank response; (—) - Corrected response using PBP, (—) -
549 Corrected response using TIS model C_0/C_{in} ; (—△—) - Dimensionless flow
550 rate, Q_0/Q_{in} . (a) number of tanks, $N = 5$, (b) number of tanks, $N = 20$. See
551 Table 2 for parameters.

552 Figure 8:

553 Comparison of PBP and TIS inversion techniques corresponding to Case 2.

554 Legend: (o)- True response of the column, C_0/C_{in} ; (◆) - Composite response,
555 C_{out}/C_{in} ; (◇) - Blank response; (— —) Corrected response using PBP, (—) -
556 Corrected response using TIS model C_0/C_{in} ; (—△—) - Dimensionless flow
557 rate, Q_0/Q_{in} . (a) number of tanks, $N = 5$, (b) number of tanks, $N = 20$. See
558 Table 2 for parameters.

559 Figure 9:

560 Comparison of PBP and TIS inversion techniques corresponding to Case 3.
561 Legend: (o)- True response of the column; (◆) - Composite response; (◇) -
562 Blank response; (— —) Corrected response using PBP, (—) - Corrected response
563 using TIS model; (—△—) - Dimensionless flow rate. (a) number of tanks,
564 $N = 5$, (b) number of tanks, $N = 20$, see Table 2 for parameters.

565 Figure 10:

566 Comparison of PBP and TIS inversion techniques corresponding to Case 4.
567 Legend: (o)- True response of the column, C_0/C_{in} ; (◆) - Composite response,
568 C_{out}/C_{in} ; (◇) - Blank response; (— —) Corrected response using PBP, (—) -
569 Corrected response using TIS model C_0/C_{in} ; (—△—) - Dimensionless flow
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574 The true and the corrected responses are shown in the main figure while
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579 **List of Table Captions**

580 Table 1:
581 Parameters for simulation.

582 Table 2:
583 Parameters for case study.

(a) Composite response

(b) Blank response

MPV- Multi-position switch valve
MFC- Mass flow controller
ZDV – Zero-dead-volume

FM – Flow meter
BPR- Back pressure regulator

Fig. 1. Simplified schematic for various experiments performed to correct for extra-column contributions.

Fig. 2. Qualitative responses for experimental configurations shown in Fig. 1 and illustration of the point by point correction procedure.

(a) Schematic of Tanks-in-series (TIS) model

(b) Modeling dispersion in extra-column volume

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(a)

(b)

Fig. 6. Inversion of the TIS model for (a) no variation of inlet flowrate and (b) with variation inlet flowrate.

(a)

(b)

Fig. 7. Comparison of PBP and TIS inversion techniques corresponding to Case 1. Legend: ($\circ$)- True response of the column, C_0/C_{in} ; ($\blacklozenge$) - Composite response, C_{out}/C_{in} ; ($\diamond$) - Blank response; (---) Corrected response using PBP, (—) - Corrected response using TIS model C_0/C_{in} ; ($-\triangle-$) - Dimensionless flow rate, Q_0/Q_{in} . (a) number of tanks, $N = 5$, (b) number of tanks, $N = 20$. See Table 2 for parameters.

(a)

(b)

Fig. 8. Comparison of PBP and TIS inversion techniques corresponding to the Case 2. Legend: (○)- True response of the column, C_0/C_{in} ; (◆) - Composite response, C_{out}/C_{in} ; (◇) - Blank response; (---) Corrected response using PBP, (—) - Corrected response using TIS model C_0/C_{in} ; (—△—) - Dimensionless flow rate, Q_0/Q_{in} . (a) number of tanks, $N = 5$, (b) number of tanks, $N = 20$. See Table 2 for parameters.

(a)

(b)

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(a)

(b)

Fig. 10. Comparison of PBP and TIS inversion techniques corresponding to Case 4. Legend: ($\circ$)- True response of the column, C_0/C_{in} ; ($\blacklozenge$) - Composite response, C_{out}/C_{in} ; ($\diamond$) - Blank response; (---) Corrected response using PBP, (—) - Corrected response using TIS model C_0/C_{in} ; ($-\triangle-$) - Dimensionless flow rate, Q_0/Q_{in} . (a) number of tanks, $N = 5$, (b) number of tanks, $N = 20$. See Table 2 for parameters.

(a)

(b)

Fig. 11. Comparison of PBP and TIS inversion techniques corresponding to Case 5. The true and the corrected responses are shown in the main figure while the composite and blank responses are shown in the inset. Legend: (o)- True response of the column, C_0/C_{in} ; ($\blacklozenge$) - Composite response, C_{out}/C_{in} ; ($\diamond$) - Blank response. (a) number of tanks, $N = 5$, (b) number of tanks, $N = 20$, see Table 2 for parameters.

Parameter	Value
Column length, L [cm]	35.00
Bed voidage of the column, ϵ	0.40
Pressure, P [atm]	1.00
Temperature, T [$^{\circ}$ C]	25.00
Henry constant, K	14.80
Solid saturation capacity, q_s [$\times 10^{-3}$ mol /mL]	5.26
Molecular diffusivity, D_m [cm ² /s]	0.20

Table 1

Parameters for simulation.

Parameter	Case 1	Case 2	Case 3	Case 4	Case 5
LDF coefficient, k [1/s]	0.100	0.010	0.010	0.010	0.001
Non-linearity parameter, λ	0.10	0.50	0.50	0.90	0.10
Inlet volumetric flow rate, Q_{in} [mL/s]	1.00	1.00	5.00	1.00	1.00
Inlet gas phase mole fraction, X_{in}	0.05	0.05	0.50	0.50	0.05

Table 2

Parameters for case study.