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The front velocity modelling approach in the chromatographic column characterization of glucose and fructose separation in SMB

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ABSTRACT

The characterization of chromatographic columns is a primary and important step in the determination of the main parameters employed in the modeling of SMB (Simulated Moving Bed) process. In this work the eleven chromatographic columns utilized in a SMB unit of glucose and fructose separation were modeled through a novel modeling approach, the *front velocity* of convection. In such a modeling approach the experimental volumetric flow rate is employed for the discretization of the volumetric elements moving along the porous column. In the new approach the convection of the liquid phase is the main phenomenon in the transport of molecules along the chromatographic column followed by the mass transfer phenomenon between the solid adsorbent and the liquid phase. The mass transfers were represented by two lumped kinetic mechanisms, without (linear type) and with maximum adsorption capacity (Langmuir type). The simulation results show good agreement between the *front velocity* modeling approach and the pulse experiments both for glucose and fructose in terms of concentration along time. The lumped mass transfer Langmuir kinetic model led to peak tailings, thus showing that not only the Langmuir isotherm can lead to such profiles, but also the linear kinetic mechanism can lead to the same chromatographic behavior. The simulation results of the new *front velocity* approach are similar to those obtained from classic convection-dispersion models with axial dispersion coefficients. Such modeling approach can be used as a powerful tool to determine the chromatographic behavior of a sample because it can be easily implemented for routine analysis and it requires a lower number of parameters.

KEYWORDS: front velocity, mass transfer, liquid chromatography, glucose, fructose, SMB

INTRODUCTION

The chromatographic column characterization is an important step in the determination of the mass transport properties which will be used later in the design of industrial units as the simulated moving bed (SMB) process. The modeling and simulation of chromatographic systems lead to the comprehension of the main mass transfer mechanisms and operating conditions that can be

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used to improve the separation/purification of molecules.

The aplication of inverse problem methodology to chromatography has proven to be important in the optimization studies as well as in the determination of mass transfer parameters with higher accuracy as attested by several researches involving the study and analysis of adsorption chromatographic systems [1-8]. In the work of Vasconcellos *et al.* [1] an inverse problem formulation with the minimization of a cost function of squared residues was applied in the mass transfer parameters estimation of the adsorption of bovine serum albumin (BSA). The optimization method used was the Levenberg-Marquardt one which was able to determine successfully the parameters of the non-linear equations. Câmara and Silva Neto [2] proposed an inverse stochastic routine similar to the traditional Luus-Jakola method to study batch and continuous solid-liquid chromatography. This method reduces drastically the window of search in the first step keeping its size a function of the domain of the unknown variables. This new inverse routine was successful in obtaining three unknown parameters of the mass transfer of the continuous chromatographic process studied. The inverse problem application in the optimization of simulated moving bed process (SMB) is the new tendency of modeling and simulation [6-8] due to the complexity of such process in the determination of the best operating conditions to achieve the highest purity of the products. Nam and Mun [7] and Nam *et al.* [8] applied the NSGA-II-JG algorithm, which is a robust optimization tool based on genetic algorithm routine. The modified genetic algorithm was applied by Nam and Mun [7] to optimize the continuous removal of acetic acid in a three-zone SMB process, whereas Nam *et al.* [8] used it to evaluate the optimal separation of phenylalanine and tryptophan through a solvent-gradient SMB process.

The chromatographic column model determines the final separation performance of the SMB as the process corresponds to a number of interconnected columns. In general, different research groups employ dispersion models [9, 10] to represent the chromatographic columns. These models are robust and efficient but need deep numerical treatment of the partial differential equations which requires high computational time. Variations of dispersion chromatographic models can be observed in the SMB studies as in the works of Horneman *et al.* [11] and Houwing *et al.* [12]. These authors employed a global mass transfer coefficient estimated from an empirical expression which is a function of the mass transfer in the liquid and solid phase. The axial dispersion was not considered in such models. A different chromatographic modeling approach has been used by Wang's group to study and evaluate the SMB process [13-15]. The authors employ the *Standing Wave Design* concept which assumes concentration profiles for each separation zone of the SMB process to achieve the desirable purities of products in both extract and raffinate. From simple algebraic equations it is possible to establish a connection between recovery and purity of the products with parameters as size of the separation zones, solid velocity, flow rate at the zones, isotherm types and also mass transfer parameters.

In this work a novel chromatographic modeling approach was proposed, the *front velocity* of convection. The *front velocity* modeling approach was studied and evaluated through the characterization of liquid chromatographic columns utilized in a SMB pilot unit of glucose and fructose separation. The simulations were compared to experimental data for the determination of the mass transfer parameters represented by two lumped mass transfer resistance models, without (linear type) and with maximum adsorption capacity (Langmuir type).

MODELLING APPROACH

The novel *front velocity* modeling approach of liquid chromatography was first proposed in 2011 by Câmara [16]. In the *front velocity* of convection the modeling approach employs the experimental flow rate of the liquid phase for the discretization of the volumetric elements moving along the porous column. In the new approach the convection of the liquid phase is regarded as the main phenomenon in the transport of molecules along the chromatographic column followed by the mass transfer between the solid adsorbent and the liquid phase. The convection of liquid phase is

considered the main phenomenon due to a flow rate driven into the column by an external pumping system. The time needed by the liquid phase to percolate the total length of the chromatographic column can be determined as the volumetric flow rate, porosity and column volume are known experimentally. In the chromatographic column shown in Fig. 1, the control volume of size J^* moves along the column with the same velocity of the eluant flow. The column length is discretized with control volumes of size J^*. The time interval (Δt) of the liquid phase to move along each control volume is obtained from Eq. 1

$$\Delta t = \frac{\varepsilon V}{n F} \tag{1}$$

in which ε, V, n and F correspond to the bed porosity of the column, the total volume of the column, the total number of control volumes and the liquid flow rate, respectively.

In the mass transfer kinetic step two lumped mass transfer models were assumed. In the first model (Eq. 2) there is no maximum capacity of adsorption (q_m) while in the second it is incorporated through a Langmuir kinetic (Eq. 3). Eqs. 2 and 3 present the lumped models in terms of rate of solute mass transfer in the solid phase. In such models the terms C, q, q_m k_1 and k_2 are, respectively, the concentration in the liquid and solid phase, the maximum capacity of adsorption and the global mass transfer kinetic constant of adsorption and desorption. The first and second lumped mass transfer models (Eq. 2 and 3 respectively) have linear and Langmuir relationships between the kinetic terms of adsorption (second term) and desorption (third term).

$$\frac{dq}{dt} = k_1 C - k_2 q \tag{2}$$

$$\frac{dq}{dt} = k_1 C(q_m - q) - k_2 q \tag{3}$$

Such kinetic models previously described at equilibrium lead to linear and Langmuir isotherms, respectively.

The simulations from the *front velocity* modeling approach were compared to the experimental data from Azevedo and Rodrigues [17]. The authors conducted pulse experiments in the eleven SMB columns placed in series using a binary solution of glucose and fructose. They employed 300 mL of samples containing 20 g/L that were injected into the set of 11 columns under a flow rate of 30 ml/min. According to Azevedo and Rodrigues [17] the eleven Superformance® glass columns (Götec Labortechnik) used in the SMB pilot unit were packed with cationic gel Dowex Monosphere 99/Ca resin (Supelco) by the slurry method. These columns (internal diameter, 2.6 cm; length, 29 cm) have a system for temperature control.

RESULTS AND DISCUSSION

Figs. 2 and 3 present the simulation results in terms of concentration along time of the linear mass transfer lumped model (Eq. 2), which were compared to the linear equilibrium condition (linear isotherm). In all simulations the experimental chromatographic operating conditions of Azevedo and Rodrigues [17] were considered. The time-step size in the *front velocity* modeling approach was assumed to be equal to 10^{-1}.

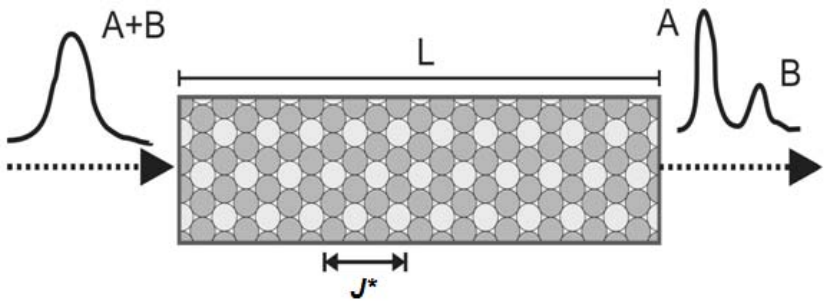

Fig. 1. Chromatographic column of lenght L with a volume of discretization of size J^*.

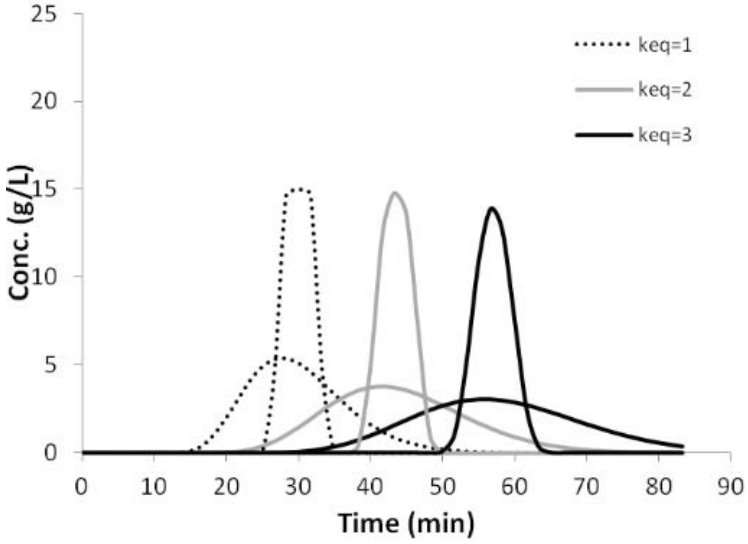

Fig. 2. Two sets of chromatograms comparing the linear mass transfer with linear equilibrium: linear isotherm effect (F = 50 mL/min, C_F = 15 g/L, V_s = 300 mL, k_2 = 0.01 min^{-1}).

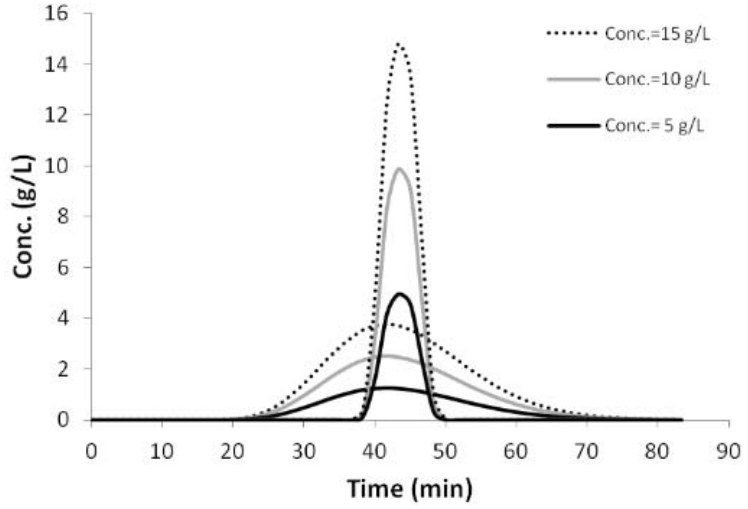

Fig. 3. Two sets of chromatograms comparing the linear mass transfer with linear equilibrium: concentration effect (F = 50 mL/min, V_s = 300 mL, k_1 = 0.02 min^{-1}, k_2 = 0.01 min^{-1}, k_{eq} = 2).

In Fig. 2 the immediate linear equilibrium (linear isotherm) of mass transfer between the solid and liquid phase corresponds to the upper curves which show symmetrical profiles without either tailing or fronting behavior. The maximum concentration of the peaks almost reached the concentration of feed (C_F = 15 g/L), showing an increase in the peak broadening with the increase in the equilibrium constant *(k_{eq})*. The term V_s corresponds to the volume of the sample. The same experimental conditions were employed for the linear lumped model (Eq. 2) with k_2 = 0.01 L/min (k_1 = k_2.keq). The simulation results from linear lumped model correpond to the lower curves which show unsymmetrical profiles with significant tailing. It can be noted that the residence times of the peaks were closer to those obtained from linear equilibrium. Also, the increase of the equilibrium constant increased the peak broadening.

Fig. 3 also presents a comparison between the linear equilibrium with the linear lumped mass transfer model as a function of the feed concentration. As can be seen from Fig. 3 the increase of the feed concentration in the condition of linear equilibrium (upper curves) lead to symmetrical profiles without increasing the chromatographic peaks. In the linear lumped model the effect of feed concentration over the peak broadening was small but increased with the increase of the feed concentration.

In Fig. 4 the linear lumped mass transfer model was evaluated through the increase of the volume of the sample for two different conditions of mass transfer kinetic constant of adsorption (k_1). The low value of k_1 leads to a signifficant effect over the chromatogram tailing (the peaks at the begining). In such conditions the value of k_{eq} corresponds to 0.2 which is lower than the one related to the chromatograms at the end ($k_{eq} = 2$).

The simulation results from the lumped mass transfer model of Langmuir kinetic (Eq. 3) are presented in Fig. 5 to 7. In Fig. 5 the effects of feed concentration were evaluated showing a net response over the peak broadening. The increase in the feed concentration leads to a significant

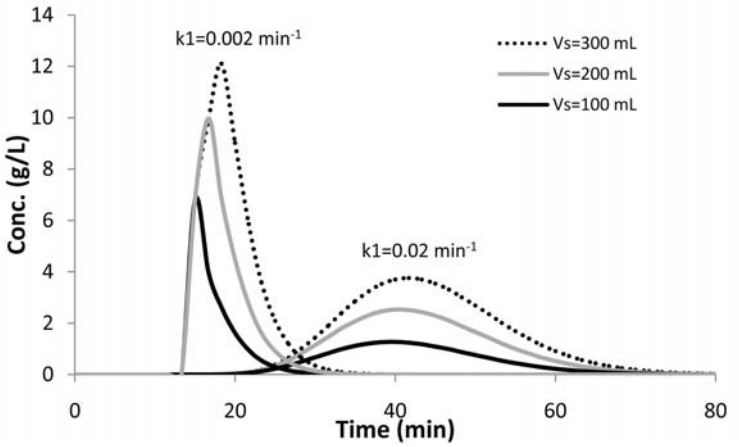

Fig. 4. Two sets of chromatograms from linear mass transfer mechanism: sample volume effect (F = 50 mL/min, k_2 = 0.01 min^{-1}).

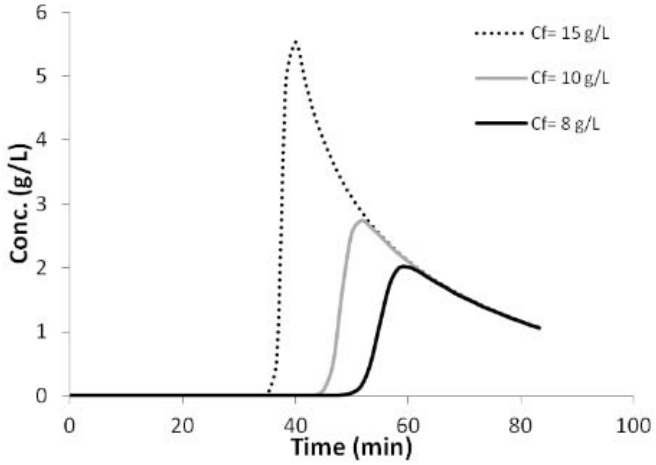

Fig. 5. Chromatograms as a function of feed concentration (q_m = 10 g/L, F = 30 mL/min, V_s = 300 mL, k_1 = 0.005 L/g.min, k_2 = 0.01 min^{-1}).

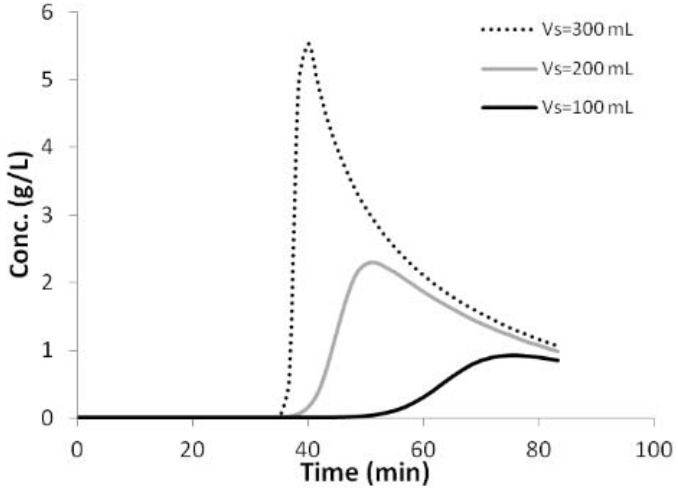

Fig. 6. Chromatograms as a function of sample volume (q_m = 10 g/L, F = 30 mL/min, C_F = 15 g/L, k_1 = 0.005 L/g.min, k_2 = 0.01 min^{-1}).

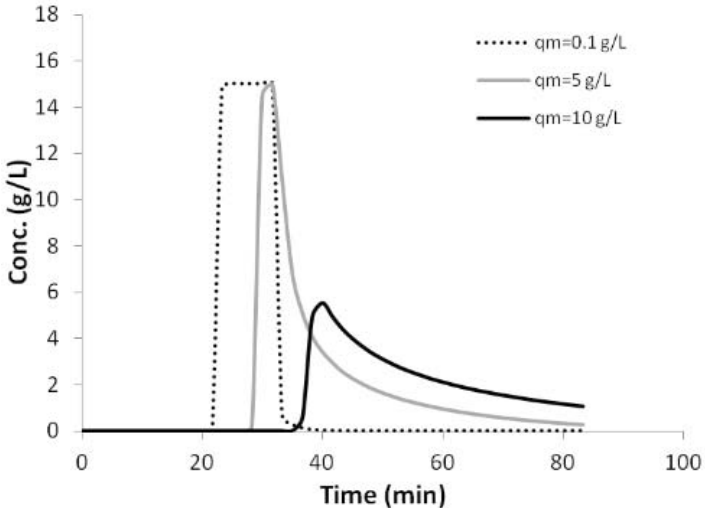

Fig. 7. Chromatograms as a function of maximum capacity of adsorption (C_F = 15 g/L, F = 30 mL/min, V_s = 300 mL, k_1 = 0.005 L/g.min, k_2 = 0.01 min^{-1}).

increase in the peak broadening. Tailing is very proeminent in such lumped mass transfer model by Langmuir kinetic. At equilibrium it leads to the classical Langmuir isotherm.

The increase in the sample volume (Fig. 7) leads to a similar effect on peak size as observed in the feed concentration effect (Fig. 6). Also, peak tailing is clearly observed. Peak tailing is a current phenomenon found in the literature when Langmuir isotherms are used in chromatographic models [18-20]. The simulation results presented in this work show that the use of lumped mass transfer kinetic models by Langmuir type also lead to the same behavior observed in the literature. Therefore, tailing cannot be exclusively related to the application of Langmuir isotherms, but also to mass transfer kinetic resistances of Langmuir type.

In the simulation results presented in Fig. 7 the chromatographic column was subjected to an adsorption overload, thus decreasing the maximum adsorption capacity of the solid adsorbent phase.

The adsorption overload is observed as the solid adsorbent becomes saturated by the molecules so the concentration measured at the column exit reaches the concentration at the column entrance (feed concentration).

The correlation between the simulation results with the *front velocity* modeling approach is shown in Fig. 8, presenting both the fit for glucose and fructose for the eleven chromatographic columns connected in series [17]. Good agreement is seen on comparing the experiments with the simulations from the new modeling approach. Both the lumped mass transfer models studied (Eqs 2 and 3) were able to represent the experimental data very well, including peak tailing in the chromatograms. There are insignificant low deviations in the correlations between lumped mass transfer model and the experimental data of glucose and fructose (Fig. 8).

In order to estimate the unknown parameters, we formulated the inverse problem implicitly as an optimization routine (cost function, R) given by the summation of the squared residues between the experimental (C_{exp}) and the calculated (C_{cal}) values of the solute concentration.

$$R = \sum_{i}^{p} (C_{exp}^{i} - C_{cal}^{i})^2 \quad (4)$$

The inverse routine utilized was the Random Restricted Window-R2W, which is a new sthocastic method proposed in 2008 by Câmara and Silva Neto [2].

Table 1 presents the mass tranfer parameters from the optimization routine applying the R2W method [2] for the two lumped mass transfer kinetic models studied. The lower values of the residue cost function (R) for both glucose and fructose when using the Langmuir kinetic indicate the greater correlation of such lumped mass transfer approaches. The correlation of the Langmuir kinetic was higher due to the lower value of residue. The *front velocity* approach by Langmuir kinetic led to very close values of maximum adsorption capacity of glucose and fructose.

The good fit of the two lumped models with the experiments can be verified in Fig. 8. Azevedo and Rodrigues [17] also achieved a very good agreement between the predicted values and the experimental ones. It must be pointed out that they employed a very robust chromatographic dispersion model with seven parameters. In the *front velocity* model approach the number of parameters are two and three for the linear and Langmuir lumped mass transfer kinetic models, respectively. Despite the differences between the *front velocity* approach and the model of Azevedo and Rodrigues [17]

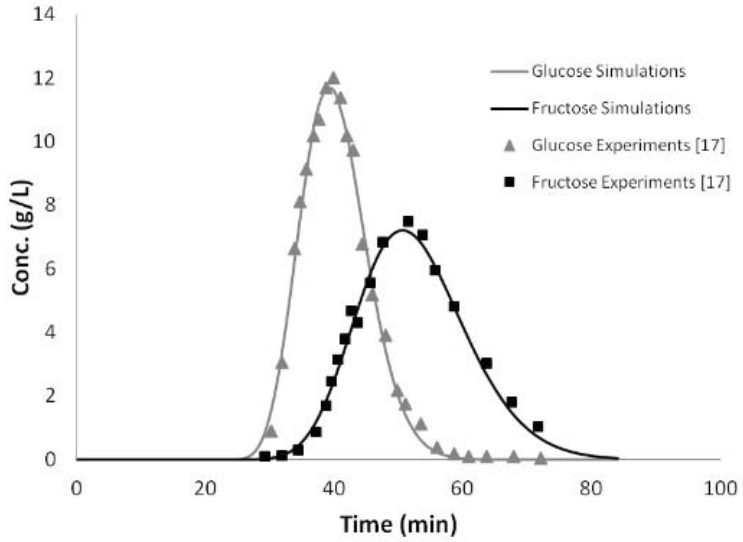

Fig. 8. Correlations between simulation results (lines) and the adsorption experimental data (points) of glucose and fructose. Experimental data from Azevedo and Rodrigues [17].

Table 1. Mass transfer parameters obtained from inverse optimization routine.

	Lumped mass transfer kinetic by			
	Linear[#1] adsorption (Eq. 2)		Langmuir[#2] adsorption (Eq. 3)	
	Glucose	Fructose	Glucose	Fructose
k_1	0.01292	0.01452	3.77.E-5	4.03.E-5
k_2	0.02362	0.01318	0.02339	0.01304
$K_{eq}=k_1/k_2$	0.54697	1.10161	0.00161	0.00309
R	3.91	1.65	3.52	1.60
q_m	-	-	343.8	361.9

[#1]Units: $k_1 = k_2 = min^{-1}$; $K_{eq} = 1$; $R = g/L$
[#2]Units: $k_1 = L/g.min$; $k_2 = min^{-1}$; $K_{eq} = L/g$; $R = q_m = g/L$

they lead to closer ratios in terms of equilibrium constants between the glucose and fructose. The values are K_{glu}/K_{fruc} = 0.527, 0.522 and 0.497, respectively obtained by Azevedo and Rodrigues [17], linear and Langmuir kinetic models.

CONCLUSIONS

The new modeling approach, the *front velocity* of convection, was able to represent very well the pulse experiments of adsorption of glucose and fructose through the eleven chromatographic columns utilized in the SMB separation unit. The use of two lumped mass transfer kinetic mechanisms with linear and Langmuir adsorptions combined with the *front velocity* approach led to chromatographic profiles which are very similar to those observed experimentally.

The employing of the lumped mass transfer model by Langmuir kinetic led to the tailing behavior of the chromatographic peaks which are related to the use of Langmuir isotherms according to the literature. Therefore, tailing cannot be exclusively related to the Langmuir isotherms, but also to the mass transfer kinetic resistances of Langmuir type. Also, the linear kinetic model led to the same behavior of the chromatorgraphic peaks.

The simulation results of the new *front velocity* approach led to similar behavior when compared to those obtained from classic convection-dispersion models with axial dispersion coefficients. Such modeling approach can be used as a useful tool to determine the chromatographic behavior of a sample because it can be easily implemented for routine analysis and it requires lower number of parameters.

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