The Front Velocity Approach in the Modelling of Simulated Moving Bed Process (SMB)

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Abstract: The Simulated Moving Bed (SMB) is a countercurrent and continuum process that presents a high separation efficiency. It has been extensively applied in the separation of the petrochemical compounds, in the enantiomeric separation of racemic drugs, and in other mixtures that are difficult to separate. Currently the models used to predict the mass transport along chromatographic columns consist of systems of partial differential equations that presents a high computational cost. To modeling SMB process the novel approach *Front Velocity* is presented. This consists of ordinary differential equations and do not utilize adsorption isotherms, and therefore it is not necessary to perform equilibrium experiments, which are common procedures in classical modeling. The first stage of the research work was to characterize the chromatographic column, where the Random constraint window (R2W) algorithm was employed associate to a kinetic mass transfer equation of the new approach in the solution of the inverse problem. With the parameters obtained in the characterization of the chromatographic column, the SMB process simulation was performed, obtaining the separation profiles of the studied compounds. To validate the model developed, the simulated results were compared with experimental data of enantiomeric separation of the Ketamine, also confronted with the simulations obtained from classical models. The results show that the *Front Velocity* model has a reasonable agreement with experimental data. Likewise showed similar results to those separation profiles obtained by classical modeling using partial differential equations, requiring computational cost about twenty times smaller.

1 INTRODUCTION

The adsorption and reaction process are adopted extensively by the food industry, textile, petrochemical, chemical and pharmacological (Gomes et al., 2002).

Therefore, many studies have been carried out with the aim of improve and create new separation techniques, and discover new substances to be used in the separation of a range of products (Zaijun et al., 2011).

Currently there are a variety of technical separation, among them, the Simulated Moving Bed (SMB), created in the sixties by the Universal Oil Products (Broughton, 1961). This process stands out for being a powerful tool to separate compounds that are very difficult to separate, as when the difference of affinity between the molecules is very small. Another positive point is that processes operates continuously requiring less solvent than batch chromatography (Gal et al., 2005). The potential of this chromatography tool has been evidenced by means of high number of studies and publications of the academic community.

The development of SMB separation processes requires a thorough study, since is necessary to determine some operating conditions such as the flow rate in each section, feed concentration and the switch time of the position of the currents (Gonçalves, 2008). The determination of the operational conditions can become a very costly to the operator of the equipment.

To resolve this issue many authors has been formulated math models capable of predicting the SMB process of separation with statistically acceptable errors compared to experimental data. According to (Antos and Seidel-Morgenstern, 2001), two different approaches, the discrete (mixed cells)

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and continuous (dispersion) models can model chromatographic columns. Currently, the models used by the researchers are robust and efficient, but they require a numerical treatment of partial differential equations, which carries a high computational cost.

In order to get a new math model to predict the profiles of separating compounds of a mixture submitted to a chromatographic separation by SMB adsorption process, the new approach called *Front Velocity* is proposed.

This approach does not require equilibrium experiments, does not need application of adsorption isotherms for characterizing the components involved in the process, and is compost for ordinary differential equations.

To validate the proposed model, it was applied in the separation of the enantiomers of ketamine anaesthetic (Santos, 2004; Santos et al., 2004) and the results were compared with those obtained by conventional models.

2 THEORY

The SMB process used by Santos in the separation of enantiomers of racemic Ketamine consists of eight chromatographic columns connected in series, divided two by two per section. Each column has 0.77 cm diameter and 20 cm in length as shown in Figure 1. The more retained enantiomer (R) is collected in the extract (Ex), while the least adsorbed enantiomer (S) is collected in the raffinate (R).

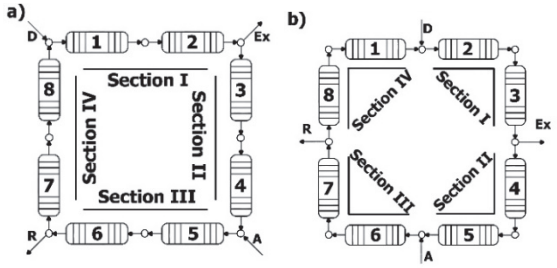

Figure 1: SMB process with two chromatography columns per section.

In the stationary and mobile phases were used, respectively, MCTA (microcrystalline cellulose acetate) and ethanol. (Santos et al., 2004) also used a HPLC (High Performance Liquid Chromatography) column, where was injected ketamine samples for calibration and determination of purity. The HPLC column used has 0.46 cm in diameter and 20 cm in length.

To represent the mass transfer, which occurs inside one chromatography column, during a separation process, the *Front Velocity* new approach was developed. This establishes that convection is the dominant phase in the solute transport along the chromatographic column. The *Front Velocity* is a discrete model (mixed cells), where the flow rate determines the liquid phase advances along the column. The rate at which the liquid phase percolates the porous column (v), is the ratio between volumetric flow rate of the mobile phase through the porous medium is described by Equation 1,

$$v = \frac{Q}{\varepsilon . A_T} \tag{1}$$

where, Q, ε and A_T represent the volumetric flow rate, porosity and the total area of the porous column, respectively (these data are obtained experimentally).

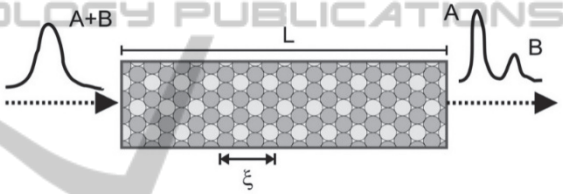

Figure 2: Chromatographic column of length L, and volume control length ξ.

To perform the calculation of the mass transfer, the chromatographic column was divided into control volumes (mixed cells) of length ξ, that moves along the column with the same speed as the eluent, as can be seen in Figure 2.

The necessary time to move the liquid phase along each control volume is obtained from Equation 2, where V is the total volume of the column and n is the number of mixed cells.

$$\Delta t = \frac{\varepsilon . V}{n . Q} \tag{2}$$

To perform the calculation of the mass transfer in the chromatography process SMB, the equations with lumped mass transfer parameter kinetics (Eqs. 3, 4) assumes that equilibrium is achieved everywhere at all times, so that the effects of axial dispersion and the mass transfer resistance were disregarded. Kinetic equations of mass transfer has been successfully employed in chromatographic processes (Câmara, 2014; Bihain et al., 2012).

$$\left(\frac{dC_i^p}{dt}\right)_\xi = -k_{ads}.C_i^p\left(qm - q_i^p\right) + k_{des}.q_i^p \quad (3)$$

$$\left(\frac{dq_i^p}{dt}\right)_\xi = k_{ads}.C_i\left(qm - q_i^p\right) - k_{des}.q_i^p \quad (4)$$

C_i^p, q_i^p, qm, k_{ads}, k_{des}, and t represent the concentration of compound i in the liquid phase at the p column, the concentration of compound i in the solid adsorbent phase at the p column, the maximum adsorption capacity, the mass transfer kinetic parameter of adsorption, the mass transfer kinetic parameter of desorption and the time, respectively. These equations (3, and 4) are applied in all mixture cells (Antos and Seidel-Morgenstern, 2001) and solved numerically utilizing a fourth-order Runge-Kutta method with a time step equal to 10–5 implemented in Fortran90.

The SMB process consists of four sections (Fig. 1), each on with different volumetric flow rate, influenced by two input streams and two output streams (feed, desorbent, extract, and raffinate). To calculate the mass transfer in each column, first is necessary determine those volumetric flow rate and after incorporate the mass balance at the entrance of each p column. After each change in the configuration of the streams (Fig. 1), the new mass balance of solutes at the nodes has to be recalculated.

As the SMB has two streams of input and two output, the overall flow is necessarily written by Eq.5.

$$Q^F + Q^D = Q^R + Q^E \quad (5)$$

To calculate the flow rates in each section and the mass balance for the first column of each section, equations 6-9 are used.

Section I:

$$Q^I = Q^{IV} + Q^D, \qquad C_{iE}^I.Q^I = C_{iS}^{IV}.Q^{IV} \quad (6)$$

Section II:

$$Q^{II} = Q^I - Q^{Ex}, \qquad C_{iE}^{II} = C_{iS}^I = C_i^{Ex} \quad (7)$$

Section III:

$$Q^{III} = Q^{II} + Q^F \quad (8)$$

$$C_{iE}^{III}Q^{IIII} = C_i^F.Q^F + C_{iS}^{II}.Q^{II} \quad (9)$$

Section IV:

$$Q^{IV} = Q^{III} - Q^R, \qquad C_{iE}^{IV} = C_{iS}^{III} = C_i^R \quad (10)$$

D, Ex, F, and R represent the desorbent, Extract, Feed, and Raffinate stream, respectively. E is the inlet concentration (concentration at the inlet of the first column of each section), S is the concentration at the last column of each section, and i is relative to the compound mixture (eg in the case of the racemic compounds, i is R or S).

3 RESULTS AND DISCUSSION

3.1 Characterization of the Chromatographic Column

A preview and important step in SMB chromatography process is the characterization of the columns, through of determination of the lumped mass transfer parameter kinetics (k_{ads}, and k_{des}). These parameters determine the rate of adsorption and desorption of molecules between the liquid and solid phases.

Table 1: Lumped mass transfer parameters obtained from the application of the inverse tool, R2W.

	S enantiomer	R enantiomer
k_{ads}	0,00218857	0,00247352
k_{des}	0,05430671	0,02700426
k_{eq}	0,04030017	0,09159742
n	505	505
q_m	29,567	29,567
R*	2,54E-05	1,87E-06

*Is the sum of squares of the residuals between the simulation and experimental data.

(Santos et al., 2004) via an analysis in a High Performance Liquid Chromatography (HPLC) system obtained the separations profiles of the enantiomers of the Ketamine. To determine k_{ads}, and k_{des} parameters, the retention times (experimental) observed in the chromatogram (Santos et al., 2004) resulting from chromatographic pulse in a HPLC analysis system were used in this study. These data were combined with mass transfer equations (Eq.3, and Eq.4) and with the inverse tool, Random Restricted Window (R2W) (Câmara and Silva Neto, 2008). The results can be seen on the table 1. The R2W is considered a simple stochastic inverse method, which uses a search algorithm with a random distribution.

In Figure 3, it is remarkable the good correlation between the experimental data (chromatogram), and

the simulation performed with *Front Velocity* approach.

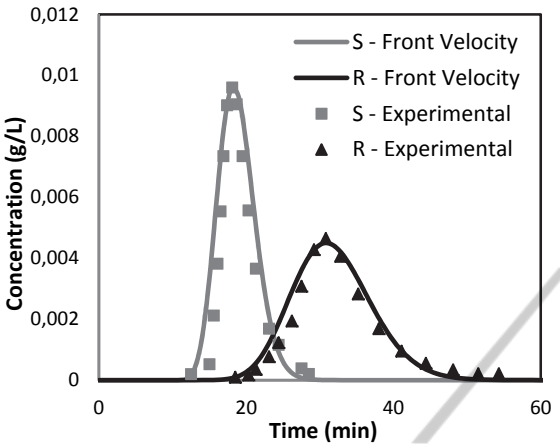

Figure 3: Chromatogram of racemic ketamine injection in the analysis column packed with MCTA; anhydrous ethanol as mobile phase, flow rate 0.25 mL/min, loop 20μl, the solution concentration 1.5 g/l. Results simulated with *Front Velocity* approach, compared to the experimental data.

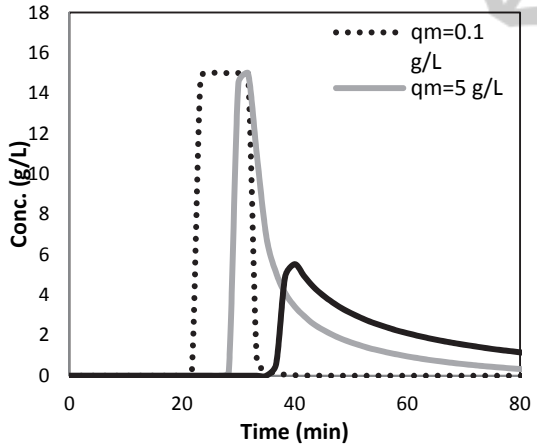

Figure 4: Variation of the maximum adsorption capacity of the adsorbent phase. $F_c = 15\ g/L, F = 30\ ml/min, Vs = 300\ ml, k1 = 0{,}005\ L/g.min, K2 = 0{,}01\ L/min$.

In a theoretical analysis performed to one chromatographic pulse as can be seen in figure 4, is observed that the novel approach presented in this work has potential to represent the resistance to mass transfer as well as the saturation of the adsorbent phase (rectangular peak). The chromatogram of the simulation also shows a peak tailing, which is a behaviour observed in the literature with the use of adsorption isotherms. Therefore, the characterization of a chromatography column cannot be linked exclusively with the isotherm application, but also with mass transfer kinetic equations.

3.2 SMB Continuous Process

With the data obtained (Table 1) in the chromatographic column characterization stage, the SMB was performed under the experimental conditions (table 2) that were determined by (Santos et al., 2004). The kinetic equations (Equations 3-4) and mass balance equations (Equations 6-9) were applied to each column of the SMB to simulate separation of the enantiomers of the ketamine, allowing the results were compared with those obtained by (Santos et al., 2004; Santos, 2004).

The equations used in the modeling of the LMS in this work, were solved numerically utilizing a fourth-order Runge-Kutta method, and implemented in Fortran 90. The total simulation time to SMB was approximately 1.5 minutes on a computer with Intel Core i5 processor (2.3 GHz) with a time step equal to 10^{-5}. The number of mixed cells (divisions of the columns) in each section is determinate by volumetric flow rate (figure 1), and it is around 300-1000 equilibrium stages as can be seen in tables Table 3.

The differential partial equations of the dispersive equilibrium model used by Santos et al. (2004), were solved by public subroutine PDECOL (Madsen and Sincovec, 1979), which implements the finite element method for spatial discretization and the ordinary differential equations were solved by GEARIB time integrator (Hindmarsh, 1976). The total simulation time was about 4 hours, using an

Table 2: Operation condition evaluations according to solvent consumption, productivity, and purity.

	Feed Concentration	Switch time (seconds)	Solvent consumption (L/g rac.)	Productivity (q.rac./D.kg)	Volumetric flow at the streams ($mL\ \mathrm{min}^{-1}$)				Purity (%)	
					Ext.	Raff.	Feed	Q_{rec}	S	R
1	1.5	1500	2.67	10.65	0.47	0.43	0.18	1.10	99.83	99.71
2	2.5	1500	1.6	17.75	0.47	0.43	0.18	1.10	99.84	99.71
3	5	1500	1.46	19.79	0.44	0.39	0.1	1.10	99.99	99.90

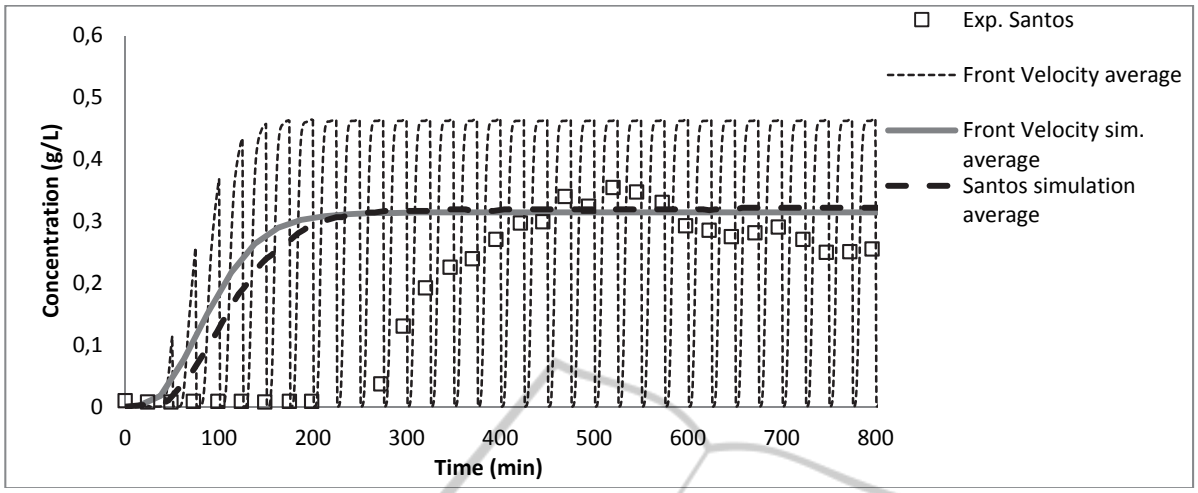

Figure 5: SMB evolution of S enantiomer concentration in the extract stream over time (transient), under experimental condition 1.

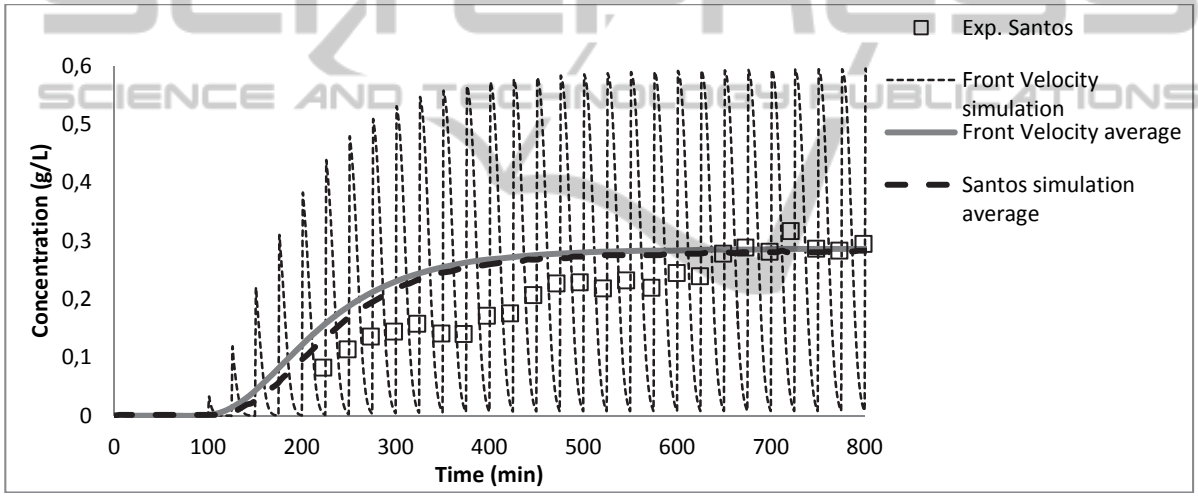

Figure 6: SMB evolution of R enantiomer concentration in the raffinate stream over time (transient), under experimental condition 1.

Intel Pentium IV (2.4 GHz) processor, with a time step equal to 10^{-5}. Each column has been divided only into 30 elements.

The good correlation between the simulation using the *Front Velocity* approach, and the classical model used by (Santos et al., 2004), over the time in the separation process can be seen in Figures 4, and 5. In addition, a comparison with the experimental data in the extract and raffinate streams can be visualized, where there is a small deviation between the simulated and experimental data while the process is still in the transient. When the process achieves the pseudo steady-state is reached a better fit.

Table 3: Number of mixed cells of the columns per section.

SMB Sections	Number of control volumes
Section I	322
Section II	562
Section III	437
Section IV	932

Figure 7 shows the concentration profiles of each enantiomer over the columns when the SMB reaches steady state. The good representation of the new approach is observed due to correlation with experimental data, and may be noted that *Front Velocity* achieves a slightly better fit compared with (Santos et al., 2004) simulations.

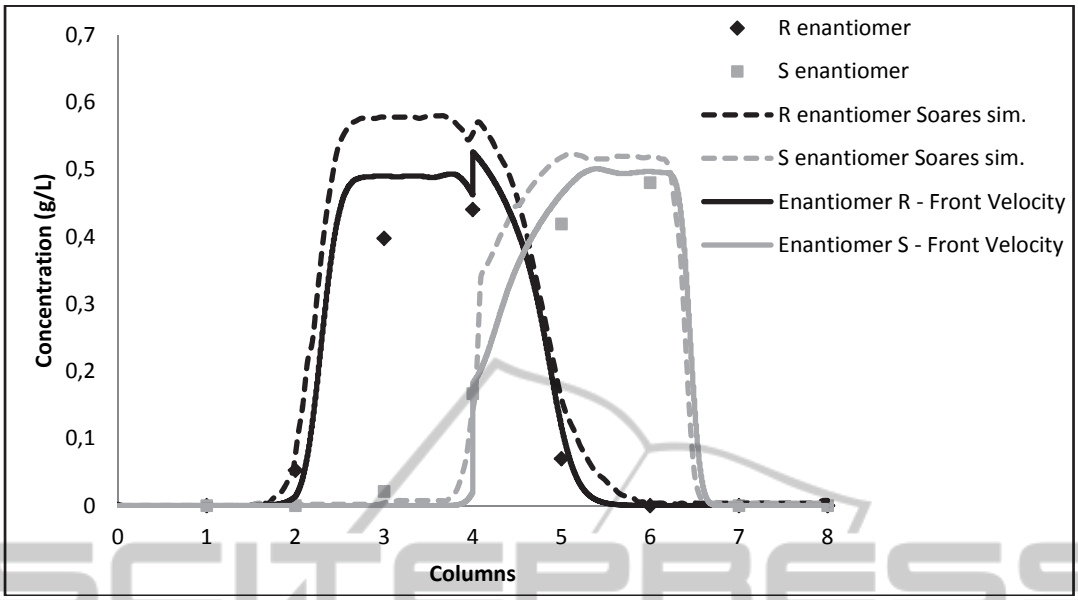

Figure 7: SMB evolution of R enantiomer concentration in the raffinate stream over time (transient).

The solvent consumption, productivity, and purity showed in table 4 were calculated with the novel approach proposed in this work. These results are very similar to experimental values (Table 2).

Table 4: The solvent consumption, productivity, and purity calculated with Front Velocity approach.

Experimental condition	1	2	3
Raffinate purity (S) %	97.72	98.84	99.89
Extract purity (R) %	99.70	99.93	99.99
Productivity (q.rac./D.kg)	10.63	17.63	19.49
Solvent consumption (L/g rac.)	2.66	1.61	1.47

4 CONCLUSIONS

A set of programs for continuous simulation of SMB process, and also to characterize the chromatographic column was developed and used under the new proposed idea of modeling the pulse experiment to determine the kinetic constants of mass transfer with mass transfer kinetic equations, instead of performing equilibrium experiments and combining them with some kind of adsorption isotherm. This procedure satisfactorily performed the separation of the enantiomers of the anaesthetic ketamine at SMB. The R2W algorithm was effective in determining the parameters of adsorption, desorption, and the maximum adsorption capacity of the adsorbent phase (k_{ads}, k_{des}, q_m).

The concentration profiles of the simulations proved to be consistent with the SMB process, and the simulated profiles of enantiomers were similar to the experimental data, showing a slightly more suiting behaviour in relation to the experimental data than the classical modeling as the model adopted by (Santos et al., 2004).

The results showed the potential of Front velocity in the prediction of the SMB separations. In a shortest time than classical models this approach performs a full simulation of the separation in a SMB process. The low computational cost is due the use the ordinary differential equations in this approach that requires less parameters than classical models, furthermore, the ease of implementation and analysis, and the need to know just few operational data of the real problem. Another relevant fact is no be necessary performing equilibrium experiments to characterize the chromatographic column.

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