

## MODELING OF SIMULATED MOVING BED PROCESSES BY THE ADSORPTION KINETIC MECHANISMS

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**Abstract.** *The Simulated Moving Bed (SMB) processes represent the actual tendency of continuous separation systems by chromatographic techniques. The modeling of such processes is crucial to the development of new technologies in the area leading to a better comprehension about the relevant aspects involved in the optimization. In this work the Simulated Moving Bed was implemented considering the kinetic mechanisms of adsorption, being it applied in the SMB configuration of 4 (four) interconnected columns. The dynamic and permanent behavior were studied through the mass balance models incorporated with different kinetic mechanisms of adsorption and desorption between the liquid and solid phase. From these aspects were observed that the respective modeling can be used effectively in the representation of such processes, being obtained a great dependence between the kinetic parameters and the maximum capacity of adsorption over the purity of the products obtained at the raffinate and extract streams*

**Keywords:** *Simulated Moving Bed (SMB), Kinetic Modeling, Adsorption Mechanisms, Chromatography*

### 1. INTRODUCTION

The chromatographic separation techniques, such as the simulated moving bed (SMB) processes, which are related to adsorption phenomena, correspond to a very important field for the separation of molecules utilized mainly by the chemical and pharmaceutical industry. The application of the modeling and simulation to study the SMB processes is a key factor for the comprehension and therefore the improvement of such systems.

The modeling of SMB systems can be done applying different mathematical approaches, with respective advantages and limitations according to the method assumed. The application of mass balance models for characterizing the transport phenomena inside the column is a constant in this area. In the modeling of SMB processes the degree of complexity may vary significantly according to the description of the unit operation (plug flow, mixture etc.), the mass transfer resistance (equilibrium, mass transfer resistance etc.) and the adsorption equilibrium (linear, Langmuir etc.) (Rodriguez and Minceva, 2005).

From the publications related to the modeling and simulation of SMB processes can be observed different research groups with different strategies of modeling. The “equilibrium theory” is an example of approach utilized to study different operation conditions of SMB processes (Mazzotti *et al.*, 1997, Gentilini *et al.*, 1998, Migliorini *et al.*, 2000 and Abel *et al.* 2002, 2004). It is interesting in the studies of optimum operation conditions of SMB systems as it simplifies the complex behavior related, generally, to non-linear competitive adsorption phenomenology (Migliorini *et al.*, 2000). The “equilibrium theory” assumes immediate equilibrium between the stationary and liquid phase, without considering the effects of axial dispersion and mass transfer resistance. The “equilibrium dispersive” models represent another path followed in the modeling of SMB processes, being observed the incorporation of linear driving force (LDF) methods to represent the adsorption of solute into the adsorbent phase (Zhong and Guiochon, 1997, 1997a, Mhlbachler *et al.*, 2001 and Pais *et al.* 1998, 1998a). In such models are considered both the axial dispersion and the convection along the column. An application of the “equilibrium dispersive” theory can be observed through the study of the effects of the columns porosity in the performance of SMB processes with and without linear adsorption conditions (Mhlbachler *et al.*, 2001). From that it was observed that the rate of production and the solute purity were affected by the fluctuations of the columns characteristics. A comparison between the separation processes by SMB and TMB (true moving bed) (Pais *et al.*, 1998) showed that to represent a TMB separation process by a SMB it is necessary to subdivide the SMB columns in a infinite number of parts with switch time close to zero. However, the results obtained with SMB and TMB were equivalent, presenting small deviation, which validate the application of SMB models in the studies of TMB processes.

The utilization of equilibrium isotherms to represent the adsorption behavior of the chromatographic columns of SMB processes is widely observed, being it related to the adsorption aspects at the equilibrium. As the SMB systems works through “pseudo-stationary” regimes, which depends on the switch time for each configuration, the adoption of models that represent the dynamic behavior of the adsorption is an important step to comprehend the separation mechanisms. In this work a SMB process formed by 4 interconnected chromatographic columns was modeled through mixture mass balance models with kinetic mechanisms of competitive adsorption. The applied modeling permitted to study the transient behavior of the SMB system through the analysis of the kinetic parameters over separation mechanisms.

## 2. PROCESS MODELING

The SMB process was represented by 4 interconnected chromatographic columns (I, II, III and IV) as shown in Fig. 1., in which F, D, R and E correspond to the flow of feed, desorbent (solvent), raffinate and extract, respectively.

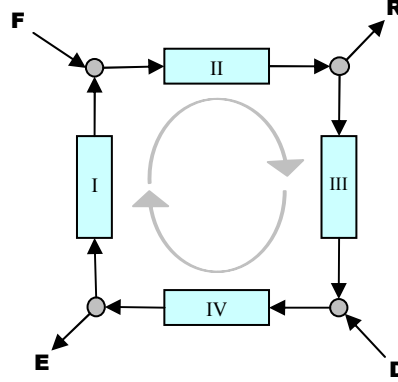


Figure 1. Representation of the SMB process

The liquid flow and the configurations of the cycle F-R-D-E-F follow the clockwise according to the switch time, which is the time spent in each configuration. As the liquid phase follows in the clockwise direction the adsorbent solid phase follows in the anti-clockwise by “Simulated” movement (SMB-*Simulated Moving Bed*).

The solutes A and B were represented as the more and less retained molecules, being determined by the following kinetic mechanisms of adsorption (Fig. 2). The mechanisms below correspond to competitive adsorption, i.e. the solutes A and B can be adsorbed by the same adsorption sites of adsorbent solid phase ( $s$ ).

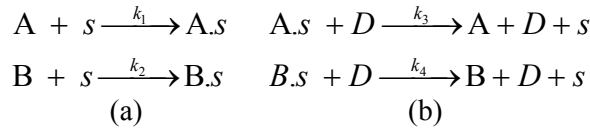


Figure 2. Kinetic mechanisms of adsorption of solutes A and B (a) with respective desorption (b)

The adsorption of solutes A and B are represented by the kinetic constants of adsorption,  $k_1$  and  $k_2$ , respectively, which depends on the solute concentration (A or B) and the concentration of adsorption sites ( $s$ ). The desorption, through the kinetic constants of desorption,  $k_3$  and  $k_4$ , for the solutes A and B, respectively, depends on the concentration of solvent (D) and the concentration of solute adsorbed on the solid phase.

According to the kinetic mechanisms shown in Fig. 2 it can be written the consumption rate of solutes A and B by the adsorbent solid phase. The consumption rate of solute A,  $(-r_A)$ , is given by

$$(-r_A) = k_1 \cdot C_A \cdot C_S - k_3 \cdot q_A \cdot C_D \quad (1)$$

where  $C_A$ ,  $C_S$ ,  $q_A$  and  $C_D$  represent the concentration of solute in the liquid phase, the concentration of adsorption sites on the adsorbent, the concentration of solute A adsorbed in the solid phase and the concentration of desorbent, respectively. Applying the mass balance models of perfect mixture (Câmara and Silva Neto, 2006) combined with the consumption rate models of Eq. 1 we determined the following equations, exemplified for the solute A.

$$\frac{dC_{A,p}}{dt} = [ c_1 \cdot C_{A0} - c_1 \cdot C_A - (k_1 \cdot C_A \cdot (q_m - q_A - q_B) - k_3 \cdot q_A \cdot C_D) ]_p \quad (2)$$

$$\frac{dq_{A,p}}{dt} = [ k_1 \cdot C_A \cdot (q_m - q_A - q_B) - k_3 \cdot q_A \cdot C_D ]_p \quad (3)$$

$$\frac{dC_{D,p}}{dt} = [ c_1 \cdot C_{D0} - c_1 \cdot C_D ]_p \quad (4)$$

with the parameter  $c_1 = Q / \varepsilon \cdot V$ , in which  $q_m$ ,  $\varepsilon$ ,  $V$  and  $Q$  correspond to the maximum adsorption capacity, the column bed porosity, the column volume and the volumetric flow, respectively. The first term of Eq. 2 corresponds to the accumulation, being the second, third and fourth the terms of solute entering, the solute exiting and the consumption rate, respectively, for each column  $p$ . More details about the application of kinetic mechanisms to study chromatographic processes can be found in Câmara and Silva Neto (2006).

Through the configuration of the SMB process shown in Fig. 1 it was obtained the global flow balance

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

, the mass balances at the alimentation node

$$Q^{II} = Q^F + Q^I \quad \text{and} \quad C_{j0}^{II} \cdot Q^{II} = C_j^F \cdot Q^F + C_j^I \cdot Q^I \quad (6)$$

, at the raffinate

$$Q^{III} = Q^{II} - Q^R \quad \text{and} \quad C_j^R = C_{j0}^{III} = C_j^{II} \quad (7)$$

, at the desorbent

$$Q^{IV} = Q^{III} + Q^D \quad \text{and} \quad C_{j0}^{IV} \cdot Q^{IV} = C_j^{III} \cdot Q^{III} + C_j^D \cdot Q^D \quad (8)$$

and at the extract

$$Q^I = Q^{IV} - Q^E \quad \text{and} \quad C_j^E = C_{j0}^I = C_j^{IV} \quad (9)$$

with the subscripts  $j$  and  $0$  related to the compounds (A, B and D) and the column entrance, respectively. The roman numbers (I, II, III and IV) correspond to each column in Fig. 1. The mass balance eqs. (6-9) must be recalculated after each clockwise change of positions F, R, D and E, having a complete cycle after the 4th change, in which the initial configuration is repeated.

### 3. RESULTS AND DISCUSSION

The simulation results presented in this article were obtained utilizing the parameters listed in Table 1 for most of the cases studied. The change of any parameter of Table 1 is incorporated in the Figure if necessary. As can be seen from Table 1, the molecule A is the more retained substance by the adsorbent phase as it has the higher kinetic constant of adsorption ( $k_1$ ). Keeping the volumetric flow of the column after the feed node, which corresponds to the Column II for the configuration of the Fig.1, we can calculate the others from the flow balances.

The system of ordinary differential equations for the mass balance models of compounds A, B and D were solved numerically utilizing the Runge Kutta's method of 4th order.

Table 1- Parameters utilized in the simulations

Maximum capacity (mg/mL)	$q_m^I$	$q_m^{II}$	$q_m^{III}$	$q_m^{IV}$
	100	100	100	100
Kinetic constants (mg/mL.min)	$k_1$	$k_2$	$k_3$	$k_4$
	10	0.5	0.8	0.4
Conc. (mg/mL)	$C_A^F$	$C_B^F$	$C_D^F$	$C_D^D$
	50	50	0	50
Vol. flow (mL/min)	$Q_F$	$Q_R$	$Q_D$	$Q_E$
	5	5	5	5
Others	e (porosity)	V(mL)	ST(min)	h (numeric step)
	0.7	40	2	0.0001

Figure 3 presents the concentrations of solutes A and B along the columns for the SMB process represented in Fig.1, showing the positions of Feed (F), raffinate (R), desorbent (D) and extract (E). As can be seen from Fig. 3 the more retained substance (A) is concentrated before the feed, at the extract (E), with the less retained (B) concentrated after the feed, at the raffinate (R). The solute B is transported by the liquid flow as this one has a weak adsorption with the adsorbent phase, being it collected at positions after the feed flow.

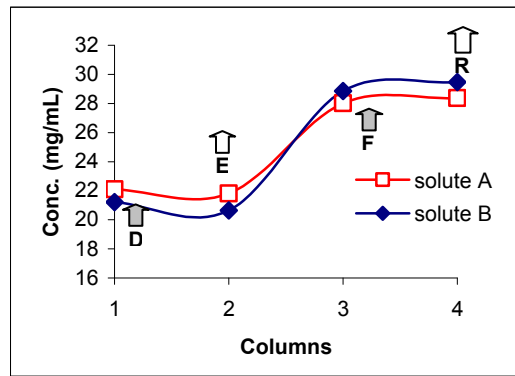


Figure 3. Solute concentrations along the columns

The respective transient behavior of Fig. 3 is presented in Fig. 4 for the concentration of solute A (Fig. 4a) and B (Fig. 4b) at the column I. From Fig. 4 can be observed the periodic aspect of the system, in which can be noted that the cyclic behavior is represented by 4 possible positions of the SMB process (vide Fig. 1).

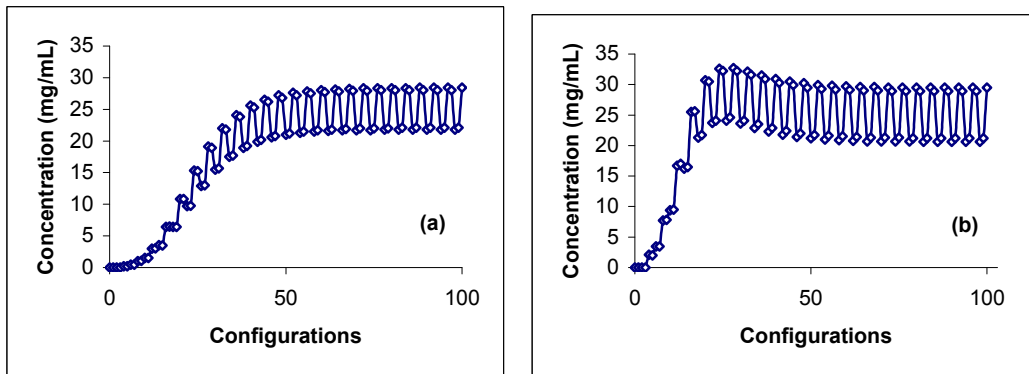


Figure 4. Concentrations profiles of solutes A (a) and B (b) at the exit of column I

The separation between the solutes A and B was analyzed through the selectivity of extract (SE) and of raffinate (SR), defined as the ratio between the concentrations of solutes A and B at the extract and the ratio between the concentrations of solutes B and A at the raffinate. Figure 5 presents the selectivity results as a function of switch time with lower (Fig. 5a) and higher (Fig. 5b) maximum capacity of adsorption. The separation process becomes interesting for selectivity values far from the unit. Comparing the results shown in Figs. 5a and 5b can be observed an improvement in the selectivity with the increase in the maximum capacity of adsorption, having an increase in the number of cycles to achieve the “pseudo-stationary” regime. The increase in the number of cycles was also followed by the increase in the optimum value of switch time (ST), leading to the increase in the separation time, which is not interesting.

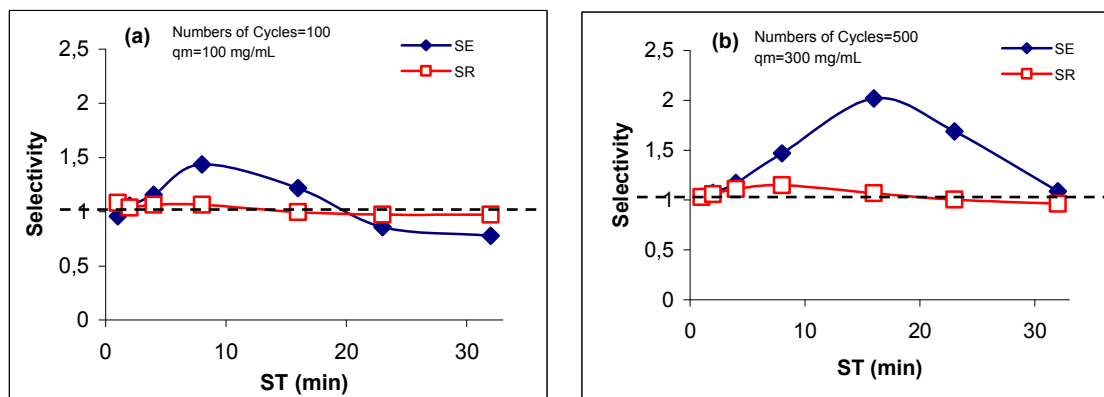


Figure 5. Selectivity as a function of switch time (ST) according to a lower (a) and higher (b) capacity of adsorption

Interesting results were obtained through the analysis of the kinetic parameters of adsorption and desorption, which are presented in Fig. 6. Varying the kinetic constant of desorption of solute A (Fig. 6a) can be observed that there is a maximum in the profile of SE; The SR have a small increased with  $k_3$ . For the solute B, varying the kinetic constant of adsorption ( $k_2$ ) can be observed an increase of SE and SR decreasing  $k_2$ , having maximum values for  $k_2=0$ . This result indicates that the lower the adsorption of the less retained solute the higher the separation performance.

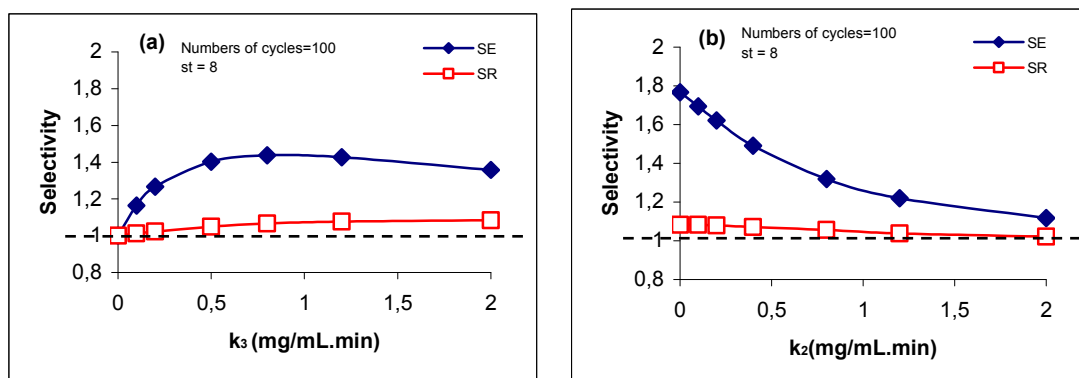


Figure 6. Selectivity as a function of kinetic parameters of desorption of solute A (a) and adsorption of solute B (b)

Better separations performances can be achieved for great values of adsorption capacity as can be verified from Fig. 7. This result showed higher values of selectivity ( $SE= 4.88$  and  $SR=4.66$ ) utilizing a maximum capacity of adsorption of  $q_m = 5000$  mg/mL.

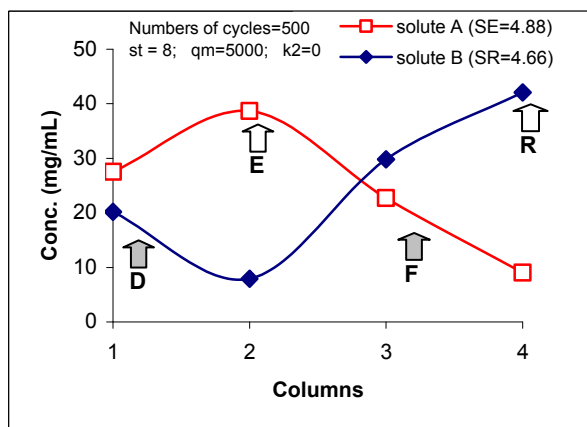


Figure 7. solute concentrations along the columns for a great capacity of adsorption

#### 4. CONCLUSIONS

From the present work of modeling of a SMB separation process by mass mixture models through adsorption kinetic phenomenology was possible to simulate the main aspects of SMB systems related to transient and “pseudo-stationary” regime. From the simulations results were observed a great dependence of the kinetic parameters and the maximum capacity of adsorption over the purity of the products obtained at the raffinate and extract. The switch time (ST) showed to be decisive to achieve the optimum conditions of separation.

The methodology of modeling for SMB processes, which can be solved from simple numeric solutions of a system of ordinary differential equations, can be used to study the complex transient behavior of the cyclic “pseudo-stationary” regime which, in general, can not be represented by a usual steady state regime.

## 5. ACKNOWLEDGEMENTS

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