ANALYSIS OF THE EFFECTS OF COLUMNS CONFIGURATIONS IN THE PERFORMANCE OF SIMULATED MOVING BED PROCESSES

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Abstract. *The Simulated Moving Bed (SMB) processes represent the actual tendency of continuous separation systems by chromatographic techniques. The configuration of chromatographic columns in the SMB processes is a new challenge, due to the high complexity, for the determination of the optimum separation conditions. The modeling of such processes is crucial to the development of new technologies in the area, which can lead to a better comprehension about the relevant aspects involved in the optimization. In this work different configurations of columns in the SMB were studied considering the modeling by kinetic mechanisms of competitive adsorption. Different aspects were studied as number of columns per section, entrance configurations, switch time, maximum capacity of adsorption etc, being determined the conditions and configurations that lead to the better conditions of separation. The column configuration showed to be so relevant in the performance of separation, presenting good conditions of separation that can be established not necessarily in the steady state. The switch time (ST), provided a strong dependence with the separation of the substances, in which was observed specific values of ST for each compound to be separated at the extract and raffinate. From the simulations were also observed 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), Chromatographic Techniques, Computational Modeling*

1. INTRODUCTION

Nowadays the pharmaceutical industry has been using with success the process in Simulated Moving Bed (SMB) for the separation of substances of high commercial value. This chromatographic separation technique, which is related to adsorption phenomena, corresponds to a very important field for the separation of molecules. The modeling of such process is very important, because it can lead to the understanding of related industrial process.

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, Mihlbachler *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 (Mihlbachler *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.

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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.

The application of kinetic mechanisms of competitive adsorption showed to be effective in the characterization of chromatographic columns used in the processes of SMB. In this work was modeled different configurations of SMB, applying the kinetic mechanisms of competitive adsorption. This approach simplifies the modeling of such separation processes, obtaining configurations of the operation systems in which the high separation performance can be reached.

2. PROCESS MODELING

The phenomena of adsorption and desorption occur simultaneously in the SMB process. The mechanisms below correspond to this competitive adsorption, i.e. the solutes A and B can be adsorbed by the same adsorption sites of adsorbent solid phase (s).

$$\begin{array}{cc} \mathrm{A} + s \xrightarrow{k_1} \mathrm{A}.s & \mathrm{A}.s + D \xrightarrow{k_3} \mathrm{A} + D + s \\ \mathrm{B} + s \xrightarrow{k_2} \mathrm{B}.s & B.s + D \xrightarrow{k_4} \mathrm{B} + D + s \\ \text{(a)} & \text{(b)} \end{array}$$

Figure 1. 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.

Figure 3 represents the mechanisms of adsorption and desorption for the solute A.

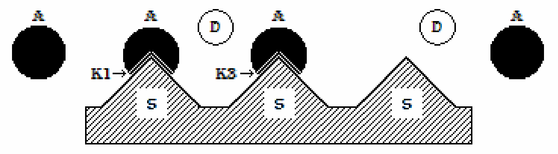


Figure 2. Mechanisms of adsorption and desorption.

According to the kinetic mechanisms shown in Fig. 1 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

$$(-r_A) = k_1.C_A.C_S - k_3.q_A.C_D \tag{1}$$

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.

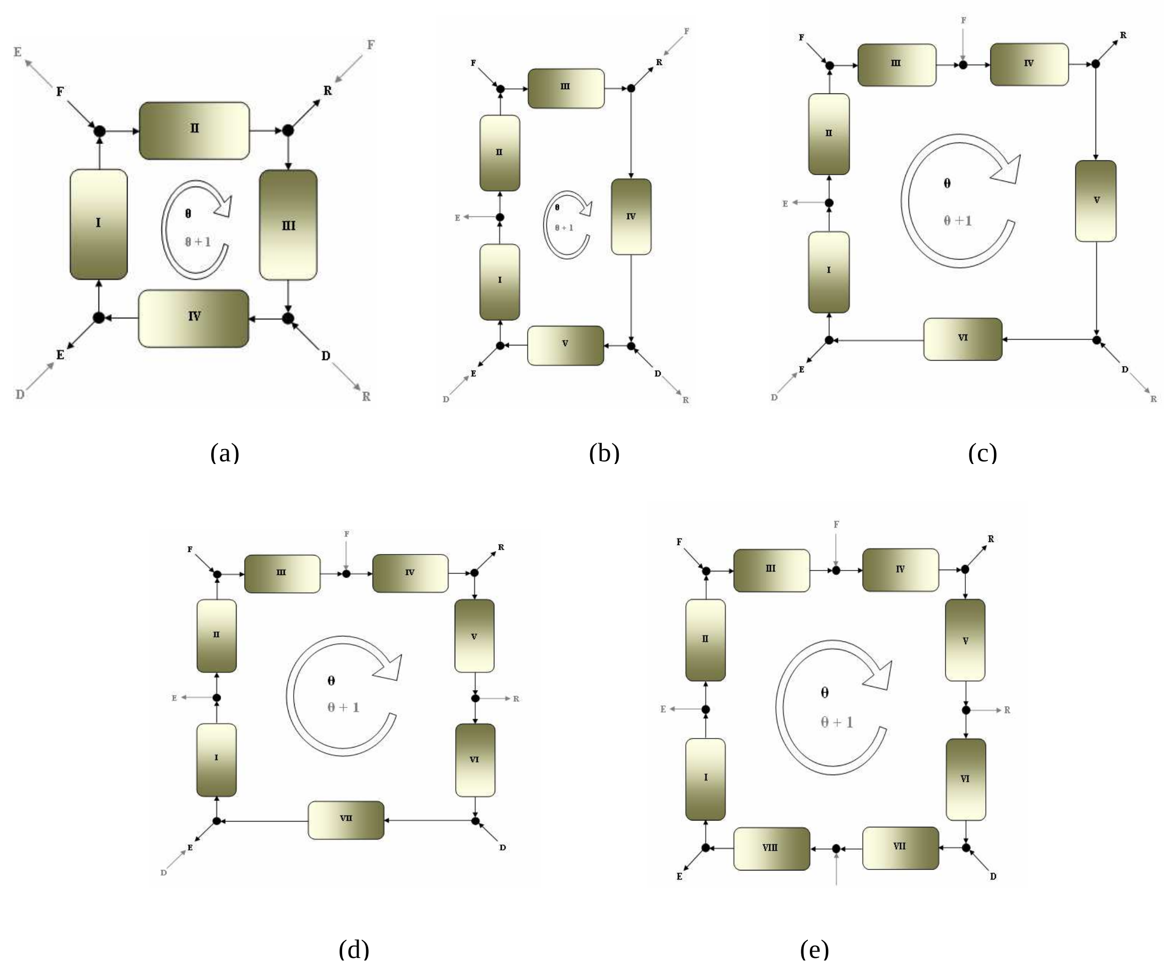
$$\frac{dC_{A,p}}{dt} = \left[\; c_1.C_{A0} - c_1.C_A - (k_1.C_A.(q_m - q_A - q_B) - k_3.q_A.C_D) \;\right]_p \tag{2}$$

$$\frac{dq_{A,p}}{dt} = \left[\; k_1.C_A.(q_m - q_A - q_B) - k_3.q_A.C_D \;\right]_p \tag{3}$$

$$\frac{dC_{D,p}}{dt} = \left[\; c_1.C_{D0} - c_1.C_D \;\right]_p \tag{4}$$

with the parameter $c_1 = Q / \varepsilon.V$, in which q_m, ε, 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).

The global flow balance for different columns configurations of SMB process was studied.



(a) (b) (c)

(d) (e)

Figure 3. 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*).

Through the configuration of the SMB process shown in Fig. 3(a) it was obtained the global flow balance

$$Q^F + Q^D = Q^R + Q^E \tag{5}$$

, the mass balances at the alimentation node

$$Q^{II} = Q^F + Q^I \quad \text{and} \quad C^{II}_{j0}.Q^{II} = C^F_j.Q^F + C^I_j.Q^I \tag{6}$$

, at the raffinate

$$Q^{III} = Q^{II} - Q^R \quad \text{and} \quad C^R_j = C^{III}_{j0} = C^{II}_j \tag{7}$$

, at the desorbent

$$Q^{IV} = Q^{III} + Q^D \quad \text{and} \quad C^{IV}_{j0}.Q^{IV} = C^{III}_j.Q^{III} + C^D_j.Q^D \tag{8}$$

and at the extract

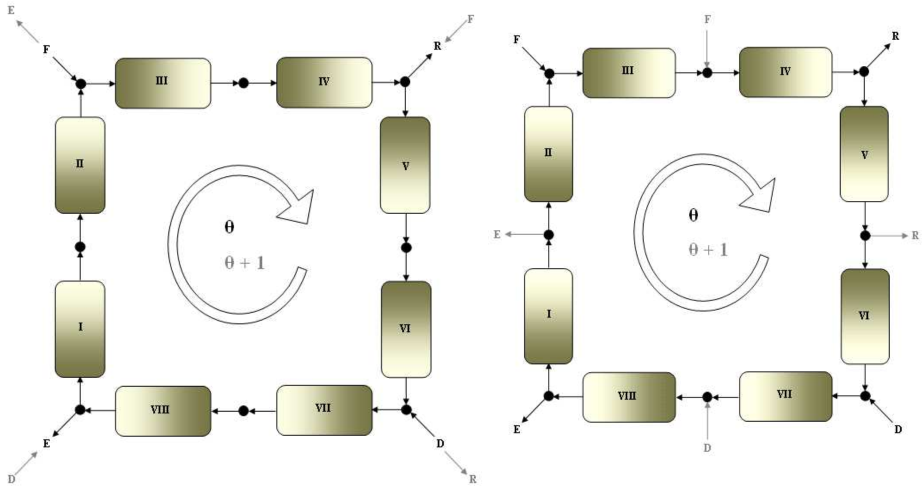
$$Q^I = Q^{IV} - Q^E \quad \text{and} \quad C^E_j = C^I_{j0} = C^{IV}_j \tag{9}$$

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 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.

Different columns configurations of SMB process as shown in Fig. 3 were implemented with different parameters of operation. The basic configuration assumed was the 1-1-1-1, which consists of only one column for each section (Fig. 3(a)), although the number of column by section was also increased until the arrangement with eight columns 2-2-2-2. The configurations studied were 1-1-1-1(Fig. 3(a)), 2-1-1-1(Fig. 3(b)), 2-2-1-1(Fig. 3(c)), 2-2-2-1(Fig. 3(d)), 2-2-2-2(Fig. 3(e)). Two differents schemes of Feed (F), raffinate (R), desorbent (D) and extract (E) were studied. The first scheme F-R-D-E was only in the edges, i. e. the nodes between the columns in each section were not used, for exemple, the configuration 2-2-2-2-A (Fig. 4(a)). The other scheme included all nodes between the columns, for exemple, the configuration 2-2-2-2-P(Fig. 4(b)). These schemes are shown in Fig. 4.



(a) (b)

Figure 4. Two different configurations of Feed (F), raffinate (R), desorbent (D) and extract (E)

The simulation results presented were obtained utilizing the parameters listed in Table 1 for most of the cases studied. With the parameters e and ST corresponding, respectively, to the porosity of the column and the swit time.

Table 1. Parameters utilized in the simulations

Kinetic constants (mg/mL.min)	k_1	k_2	k_3	k_4
	10,0	0,0	0,8	0,4
Conc. (mg/mL)	C_{AF}	C_{BF}	C_{DF}	C_{DD}
	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)	q_m (mg/mL)
	70%	40	8	5.000

Figure 5 presents the concentrations of solutes A and B along the columns for the SMB process represented in Fig. 3(a), showing the positions of Feed (F), raffinate (R), desorbent (D) and extract (E). As can be seen from Fig. 5, 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.

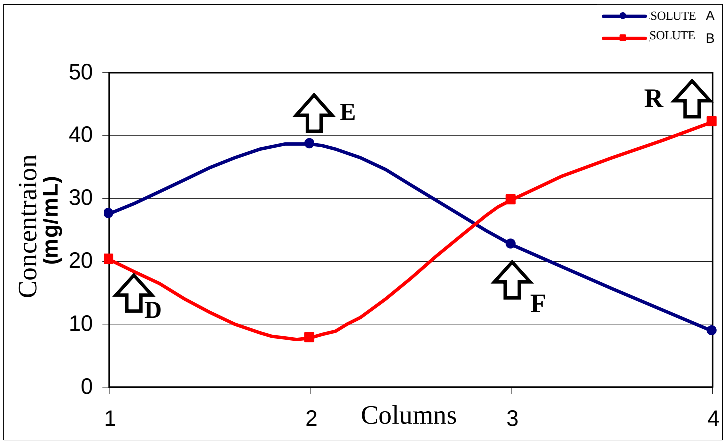


Figure 5. Solute concentrations in the liquid phase along the columns (1-1-1-1).

A qualitative comparison was done with the experimental result as shown in Fig. 6. The results, the simulated (Fig. 6a) and the experiment (Fig. 6(b)), shows the pseudo-stationary of such processes is achived after a number of cyles.

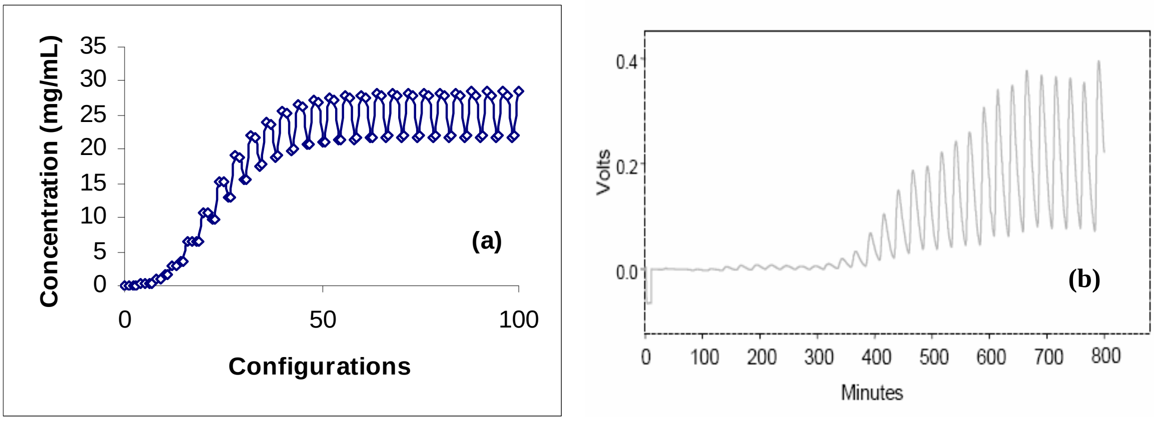
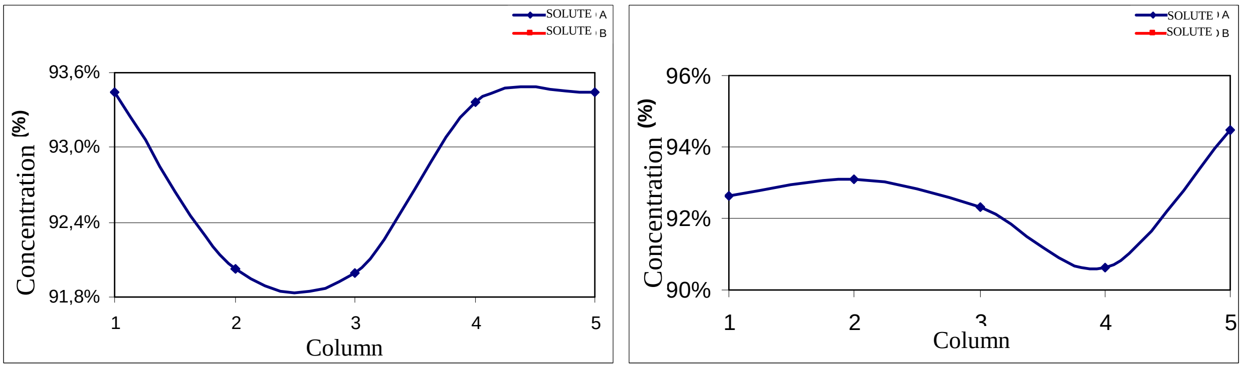


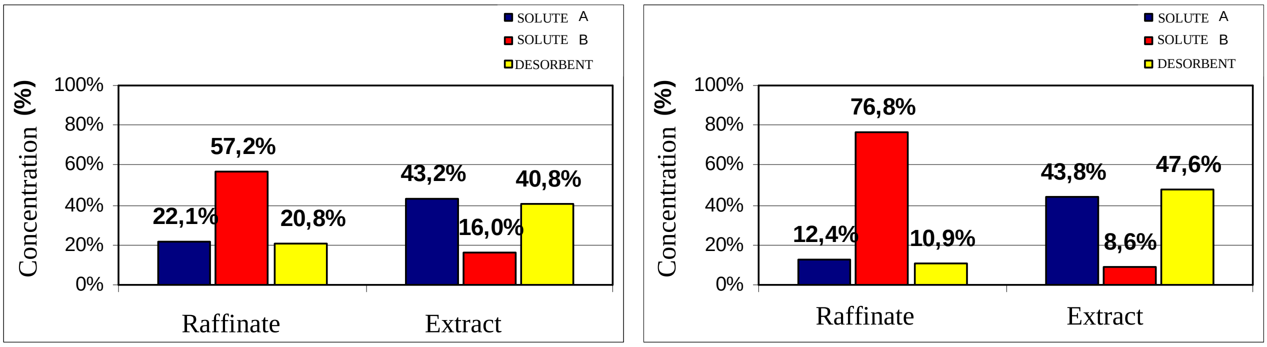
Figure 6. Comparison between the simulation and the experimental result from Santos et al. (2004).

Worse results can be shown with the scheme F-R-D-E in the "edges" when compared to the schemes F-R-D-E using all nodes between the columns. Figure 7 shows that the sorbent was more saturated in the arrangement 2-1-1-1-A, which led to low efficiency in the separation of solutes and the scheme F-R-D-E in the "edges". In general, this loss of efficiency was noted in all arrangements in which they worked only the "edges" while, by including the nodes between the columns, productivity increased with the addition of more columns in the sections of the SMB. It can be explained by the fact that the desorbent don’t acts directly in the middle columns accumulating the solute in the sorbent.



(a) (2-1-1-1-A) **(b)** (2-1-1-1-P)

Figure 7. Saturation of sorbent.



(a) (2-1-1-1-A) **(b)** (2-1-1-1-P)

Figure 8. Raffinate and extract concentrations.

Despite most cases works on a stationary state, a better separation of solutes A and B occurs during the transient state. After 200 cycles, approximately, on the stationary state the concentration of solute A increases, then, the separation is more difficult.

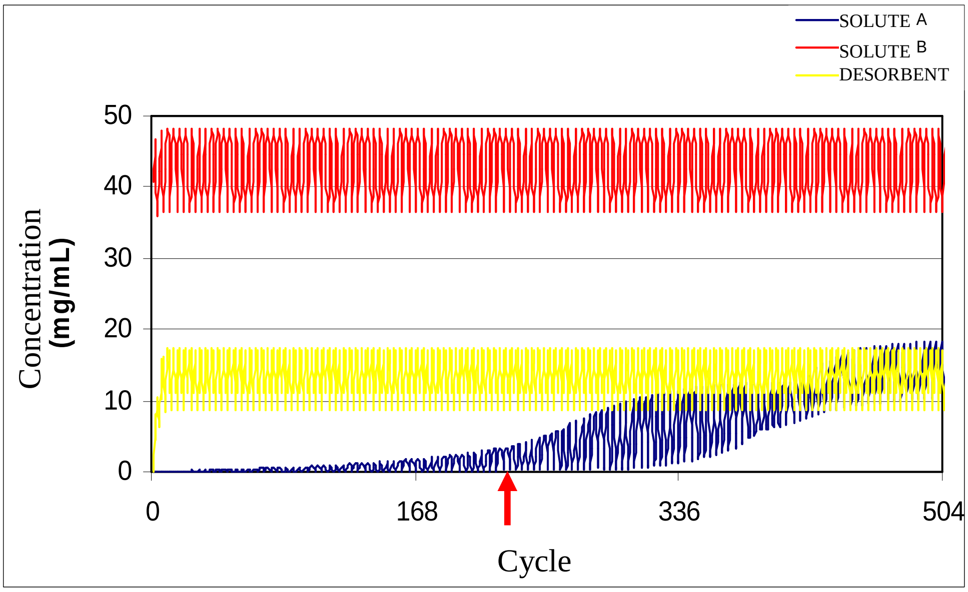


Figure 9. Solute and desorbent concentrations (2-1-1-1-A).

The configuation 2-2-2-2-P presented a better performance compared to all others configuration and scheme of F-R-D-E. The number of columns in each section is directly proportional to the efficiency of the process when the scheme F-R-D-E is in all nodes.

A second simulation showed that kinetic constants and the porosity of the column also influence the performance of separation. Utilizing a higher swit time, with the increase in porosity (90%) and constant kinetic of desorption (k_3=10 and k_4=0), best results were obtained. Figure 10 shows that the concentration of solute reached the mark of 86.6% in raffinate, while the solute only 6.5%. It shows also that not only the number of columns, but the constant kinetic influence substantially in the process of adsorption.

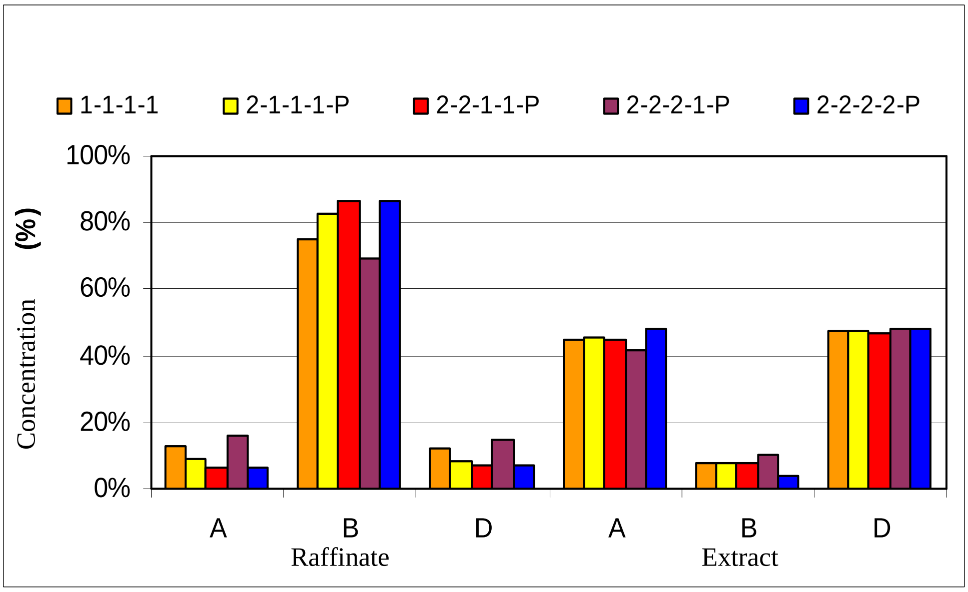


Figure 10. Raffinate and extract concentrations.

4. CONCLUSIONS

Through the kinetic models with the phenomena of mass transport can be observed that the results are optimized with the insertion of columns in the sections of the SMB.

Not only the number of columns affects the results, but the constant kinetic influence in the process of adsorption. The greater the difference of the kinetic constants between k_1-k_2 and k_3-k_4 promote a better separation of solutes.

The representation of concentration by a mass balance at the entrance and exit of each column create a system of ordinary differential equations, which, in view of other models, is a more simplified offering a easy assimilation and implementation, so the computer simulation is simplified.

Finally, the results described here represent only a small part of the possibilities that this approach provides. There is a variety of settings and parameters that can be simulated and results processed, incorporating thus valid information to the limited literary collection of this technology.

5. ACKNOWLEDGEMENTS

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