

## Solution of an Inverse Problem in Continuous Chromatography with the Generalized Extremal Optimization Algorithm

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### Introduction

The chromatographic separation processes, which involve the adsorption phenomenon, correspond to a very important approach for separating substances with high aggregated value, being utilized mainly by the chemical and pharmaceutical industry. The application of modeling and simulation in the study of such separation mechanisms is a key factor for the understanding and therefore the improvement of such systems.

Among the models of mass transfer kinetics in chromatography, the LDF (Linear Driving Force) and the Langmuir are the most important, being both related with a kinetic of first order [1]. The publication of Thomas [2] corresponds to a precursor work following the simple adsorption kinetic of Langmuir. Following the same adsorption methodology, Chase [3] derived an analytical form for the breakthrough curve, being it identical to the Thomas's model.

The application of the inverse methodology to study the chromatographic systems is a new promising area for obtaining the models parameters from the experimental data [4, 5], having a large range of applications [6, 7].

In this work the continuous mass balance models with the kinetic mechanisms of adsorption and desorption were analyzed through a inverse problem by the Generalized Extremal Optimization Algorithm (GEO).

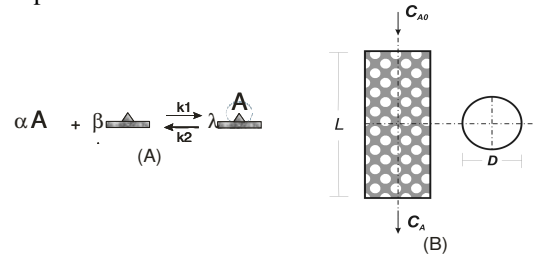
### Modeling of the direct problem

The modeling of the chromatographic separation process is based on the adsorption kinetic mechanisms over a solid surface as represented in Fig. 1A. In Fig. 2B is represented the column modeled, in which  $C_{A0}$  and  $C_A$  represent the initial concentration of solute A at the column entrance and the solute concentration at the column exit, respectively. The rate of consumption of solute A ( $-r_A$ ) is determined by

$$-r_A = k_1 \cdot C_A^\alpha \cdot C_s^\beta - k_2 \cdot q_A^\lambda \quad (1)$$

in which  $C_A$ ,  $C_s$  and  $q_A$  represent the concentration of solute in the liquid phase, the concentration of active sites of the adsorbent and the concentration of solute A adsorbed in the solid phase, respectively. The parameters

$\alpha$ ,  $\beta$  and  $\lambda$  represent the stoichiometric coefficients of the adsorption mechanism



**Figure 1- Mechanisms of adsorption (Fig. 1A) and the column representation (Fig. 1B)**

Equation 1 is converted into Eqs. 2 and 3, for the concentration of solute in the liquid and solid phase, respectively,

$$\frac{dC_A}{dt} = c_1 \cdot C_{A0} - c_1 \cdot C_A - [k_1 \cdot C_A \cdot (q_m - q_A)^2 - k_2 \cdot q_A] \quad (2)$$

$$\frac{dq_A}{dt} = k_1 \cdot C_A \cdot (q_m - q_A)^2 - k_2 \cdot q_A \quad (3)$$

with the parameter  $c_1 = Q/\varepsilon V$ , in which the parameters  $\varepsilon$ ,  $V$  and  $Q$  correspond to the porosity, the volume and the volumetric flow, respectively.

The system of Eqs. 2 and 3 was solved numerically applying the Runge-Kutta method of 4<sup>th</sup> order.

### Inverse problem modeling - GEO Algorithm

GEO is an optimization algorithm [6] inspired by a simplified evolutionary model, developed to be easily applicable to a broad class of nonlinear constrained optimization problems, while having only one free parameter ( $\gamma$ , please see Fig. 2) to be adjusted. The design variables are coded in a binary string, in which the number of bits used to encode each variable was defined in function of its required precision.

### Results

Figure 3 presents the results of the correlation between the experimental data [8] and the model (Eqs. 2 and 3) applying the GEO inverse routine.

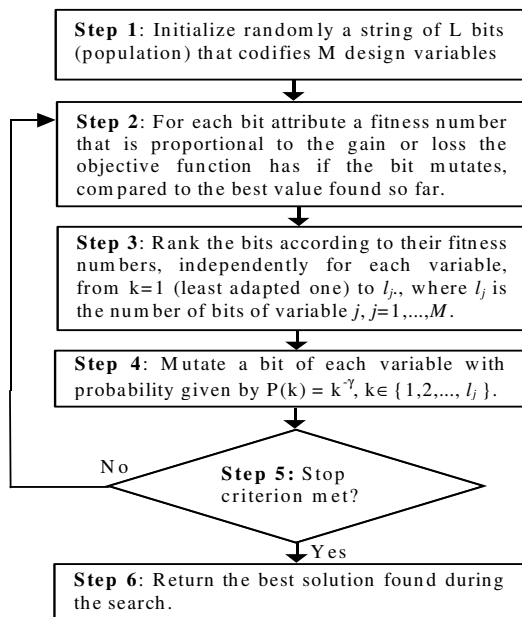


Figure 2- The canonical variant of GEO

From Fig. 3 can be observed that GEO was effective in fitting the model to the experimental data. This result shows that the model was representative in the adsorption step, being not satisfactory for the desorption one (after 128 min). The experimental parameters correspond to  $\varepsilon = 0.557$ ,  $C_{A0} = 11.5$  mg/mL,  $Q = 0.35$  mL/min and  $V = 1.57$  mL. The optimized condition encountered by GEO for the adsorption step was  $k_1 = 2.65 \cdot 10^{-4}$  mL<sup>2</sup>/mg<sup>2</sup>.min and  $q_m = 373.3$  mg/mL, applying the cost function,  $F = \sum_{i=1}^N (C_{cal_i} - C_{exp_i})^2$ , with the values  $7.02 \cdot 10^{-5}$  and 10.22 for the standard deviation and  $F$ , respectively.

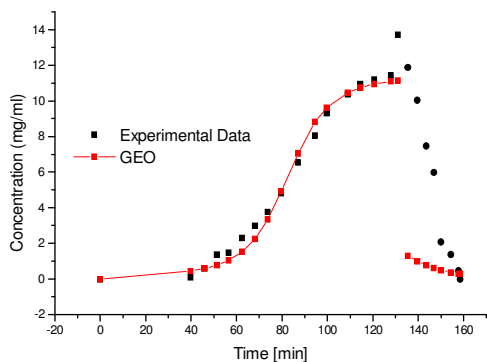


Figure 3- Concentration profiles in the adsorption and desorption steps [8]

The poor agreement observed in the desorption step is probably related to a kinetic mechanism that is not the same as the adsorption one. From the experimental data it

can be noted that in the desorption step there is a discontinuous change in the concentration with a maximum. The discontinuous change is due to a change in the solvent, which is substituted by a strong desorbent that leads to a quick desorption of the solute molecules. This change in the characteristics of the solvent leads to a change in the desorption kinetic mechanism, which is not the same as the adsorption one.

## Conclusions

The inverse routine GEO was effective in fitting the model to the experimental data. The model correlated effectively in the adsorption step, having a poor behavior in the desorption step. The poor behavior in the desorption step is probably related to the kinetic mechanism of desorption, which is different from the adsorption one.

## Acknowledgements

The authors acknowledge the financial support provided by CNPq, CAPES and FAPERJ.

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