

Towards an Efficient Mathematical Procedure for Calculating Dynamic Adsorption Process

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Abstract

The aim of this work is to obtain efficient procedures to solve dynamic liquid adsorption problems. In the design of such processes, the adsorption equilibrium relationship must be available and easily implemented in the model equations. Therefore, some modifications in the mathematical model were proposed in order to allow the use of any relation describing the equilibrium between the pore liquid and the solid phase. The methods of characteristics with appropriated boundary and initial conditions and of orthogonal collocation coupled with the DASSL routine were used for solving the process model. It was shown that the transformations and modifications proposed did not change the response of the model and enabled the improvement of the numerical solution. Two other numerical methods were used, both using the Finite Elements Method (FEM) on space discretization, and for time domain one used the Crank-Nicholson Method (CNFEM) and the other one used the 4th Order Runge-Kutta Method (RKFEM).

Keywords: adsorption, liquid mixture, simulation, fixed-bed, numerical methods

1. Introduction

The fixed bed adsorption process is complex because it deals with diffusional, thermodynamics and kinetics aspects of one fluid/solid interface that produces a large amount of parameters and variables to be studied. In the modelling and simulation of such processes, it is essential to know the adsorption equilibrium of the single solute to be removed or of the mixtures to be separated. However, accurate and complete experimental data are scarce and difficult to obtain for multicomponent adsorption, and only very limited data are available even for binary systems. Models describing fixed and simulated moving beds have been published for liquid mixtures. In this work, numerical methods, different isotherms and the development of a software were carried out in order to be possible to take decisions in relation to the evaluation of an operating adsorber or to the possibility to apply this separation process for recovering a given component from a mixture.

Several works can be cited in the literature, however, all of them dealing with specific developments. Santacesaria et al. (1982) present material balance equations for single and binary mixture adsorption. Khan et al. (2000), through thermodynamic assumptions

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and extensive analysis of liquid adsorption isotherms for various solutes and adsorbents, developed a single solute liquid adsorption isotherm. Teoh et al. (2000) developed a detailed mathematical model of dynamic high performance liquid chromatographic column. Karlsson et al. (2000) developed the optimization of the operation of a sequential – simulated moving bed separation process using MINLP. Teoh et al. (2001) developed a dynamic modeling of chromatographic process through a systematic and procedure for isotherms determinations and Lim et al. (2003) developed a generalized adsorption rate model based on the limiting component constraint in ion exchange chromatographic separation for multicomponent systems.

2. 2. Model Development And Solution

For describing the adsorption of solutes from a flowing liquid stream into a fixed bed of particles, the pore diffusion model was used. In this formulation, two mass transfer processes were considered: the external mass transfer from the bulk liquid phase to the particle surface and the internal pore diffusion within the adsorbent particle itself. The following essential assumptions were taken into account: a) diffusion coefficients independent of the mixture composition; b) spherical adsorbent particles with uniform sizes; c) constant temperature and porosity. The material balance equations for single solute adsorption were those proposed by Santacesaria *et al.* (1982), but not including axial dispersion. The model can be described through equations 1 and 2, respectively:

- fluid phase equation:

$$\varepsilon_e \frac{\partial c_{ej}}{\partial \tau} + v \frac{\partial c_{ej}}{\partial Z} = -K_L \frac{3}{R_p} (c_{ej} - c_{ij})(1 - \varepsilon_e) \quad (1)$$

- solid phase equation:

$$\varepsilon_i \frac{\partial c_{ij}}{\partial \tau} = K_L \frac{3}{R_p} (c_{ej} - c_{ij}) - \rho_s (1 - \varepsilon_i) \frac{\partial q_j}{\partial \tau} \quad (2)$$

where: - $\varepsilon_e, \varepsilon_i$ = bed and particle voidage ; - q = amount of solute adsorbed on the solid surface ; - R_p = particle radius ; - τ = time ; - v = superficial velocity of liquid ; - K_L = overall mass transfer coefficient.

The equation terms were converted into dimensionless form. The new variables and the lumping parameters are found in Scheer et al. (2001). The new forms of equations (1) and (2) are coupled by an adsorption isotherm which includes the effect of the adsorbent. To solve this system, it is necessary to differentiate the isotherm equation, an operation that requires a large amount of algebraic manipulations. So, in this work, it was adopted the same variable change proposed by von Meien and Biscaia (1994), which changes the original system of partial differential equations into a differential-algebraic one. So, the differentiation of the adsorption isotherm is not necessary anymore. For the solution of the asymmetric problem, in which the polynomial interpolation for all domain of the spatial variable produces typical oscillation of

polynomial approximations, the characteristic method is applied according modifications proposed in Mitchel and von Meien (2000).

The resulting differential-algebraic system was solved along variable j using the DASSL routine (*Differential/Algebraic System Solver*). The numerical solution provides the concentration of the solute in a chosen collocation point and the results are obtained using eight internal points of collocation for spatial coordinate approximation. For each isotherm equation, the breakthrough curve at the end of a simulated adsorption column ($z = 1$) is obtained. The characteristics and dimension of the fixed bed adsorber were maintained constant for all simulations.

3. Adsorption Isotherms

Four isotherms were tested in the proposed model for single component adsorption. The first one (equation 3) was the vacancy solution theory proposed by Suwanayuen and Danner (1980), modified by Fukuchi *et al.*, (1982) which replaces the “vacancy” spaces with water molecules. This adsorption isotherm equation for a dilute aqueous solution containing a single solute j is, as follows:

$$c_{ij} = \left[\frac{1}{K} \frac{q'_j}{1 - q'_j} \right] \left[A_{12} \frac{1 - (1 - A_{21})q'_j}{A_{12} + (1 - A_{12})q'_j} \right] \exp \left[- \frac{A_{21}(1 - A_{21})q'_j}{1 - (1 - A_{21})q'_j} - \frac{(1 - A_{12})q'_j}{A_{12} + (1 - A_{12})q'_j} \right] \quad (3)$$

Where A_{12} and A_{21} are the Wilson parameters for interaction between solute and solvent in the adsorbed phase.

When these parameters are equal to unity, equation 3 reduces to the Langmuir isotherm. The second isotherm was an empirical correlation and it has the following form (Khan *et al.*, 2000):

$$q'_j = \frac{1}{2K_1} \ln \frac{a_1 + c_{ij} \exp(K_1)}{a_1 + c_{ij} \exp(-K_1)} \quad x = w \exp \left[(1 - w)^2 (a_2 + a_3 w + a_4 w^n) \right] \quad (4 \text{ and } 5)$$

where a_1 , c_{ij} and K_1 are the constants for each isotherm. The third one was the equilibrium relationship that applies the principle of solution thermodynamic based on the equality of the fugacities of the solute in the two phases (Khan *et al.*, 2000).

Usually, data on the amount of liquid adsorbed are available in units of mol/kg and solute concentration in mol/m³. For such data, the weight fraction (w) and the mole fraction of solute in the liquid phase (x), were calculated, respectively, from the following relations:

$$w = \frac{Mq}{1000 + Mq} \quad \text{and} \quad x = \frac{c_{ij}}{c_{ij} + \rho_w \left(1 - \frac{c_{ij}}{\rho_A} \right)} \quad (6)$$

where M is this molecular weight of adsorbate; ρ_w is the molar density of pure solvent; ρ_A is the molar density of pure liquid solute at the temperature of interest. The fourth one was the correlation obtained by Khan *et al.* (1997) for pure component adsorption isotherms as following:

The fourth one was the correlation obtained by Khan *et al.* (1997) for pure component adsorption isotherms as following:

$$q'_j = \frac{a_5 c_{ij}}{(1 + a_5 c_{ij})^d} \quad (7)$$

In the above equation, when d is equal to unity, it is reduced to the Langmuir isotherm and when large values of c_{ij} occur, it is reduced to the Freundlich isotherm.

Plotting dimensionless concentration in function of time (breakthrough curves) for 2 – propanol at 25°C, using activated carbon as adsorbent and analysing the curves according to the four isotherms studied, it is verified that the curves using equations 3 and 4 show deviation from the two others. This behaviour is in agreement with the results obtained by Khan *et al.* (2000). They stated that their developed model (equation 5) outperformed the others and showed the smallest deviation between predicted value of solute concentration and the experimental value. Equation 7 was the next one in accuracy. The numerical solution allowed the prediction of the concentration at the end of the column in a simpler and more flexible model, which can easily incorporate any isotherm, even those more predictive.

4. Application of Finite Elements Methods (FEM)

The approximated solutions for the liquid adsorption problem in its variational formulation are built in the finite dimensional subspace of admissible functions, which satisfy the homogeneous contours conditions and are smooth enough to well define the integrals in a variational problem, also allowing the first derivatives to become square-integrable (Vargas et al., 2002). A partition is introduced in $[0, L]$ interval, resulting in n sub-intervals, where one Finite Element involving two nodes, i and j , is built to solve the problem, by using piecewise linear functions for the interpolation inside the k element. After applying interpolations and doing manipulations we reach:

$$M^k \frac{\partial C_e^k}{\partial t} + K^k C_e^k - F^k = 0 \quad (8)$$

where M^k , K^k , C_e^k and F^k are matrices and vectors formed by the components m_{ij} , k and f , with values varying between 1 and n for i and j for k element.

For the final construction of the global matrix, a boolean matrix L_k representing the incidence relation of element k was used and the global system of differential equations is obtained:

$$M \frac{\partial C_e}{\partial t} + K C_e - F = 0 \quad (9)$$

Many integration techniques can be used to solve time domain problems. For the CNFEM application on this model, expression (9) is assumed as:

$$[A] \{C_e\}^{t+\Delta t} = [B] \quad (10)$$

where

$$[A] = \left[\frac{2}{\Delta t} M + K \right] \quad \text{and} \quad [B] = \left[\frac{2}{\Delta t} M - K \right] \{C_e\}^t + 2[F] \quad (11)$$

In this study, the matrix are calculated once for each t moment, obtaining $C_e(t)$. Then c_p is calculated with CNFEM for each t moment. After that, the calculation follows an iterative process. For the RKFEM application, the same process was used, but the matrices were calculated at each RKFEM phase. The numerical results presented are

based on the comparison with Santacesaria experimental results (Santacesaria et al., 1982) for the m-xylene component. The following parameters were considered for this specific problem

$$T = 9600s, L = 40cm, D_L = 1.29E-2, \varepsilon_e = 0.42, \varepsilon_i = 0.2, R_p = 6.5E-2, v = 1.98E-2,$$

$$\rho = 1.4E3, a = 4.2L/mol, K_L = 1.09cm/s, q_m = 1.75E-3, c_e^f = 78E-2.$$

The results generated by CNFEM are shown in Figure 1. Each graphic represents the space discretization refinement for a stipulated time increment. For the CNFEM, time increments of 200, 100, 25 and 12.5 seconds were studied and space refinements were obtained for 10, 20, 40 and 80 elements. It can be noted that time increments of 200s and 100s for CNFEM are those that better fit with experimental data. (for RKFEM, time increments of 100, 50, 25, 12.5 and 6.25 seconds were studied and space refinements were obtained for 10, 20 and 40 elements. 100s for RKFEM is the best fit to the experimental data. The oscillations tend to disappear when mesh refinement is improved. Both models showed the same behaviour, but trying to reach an acceptable error level for the problem, the analyses indicate that CNFEM was more appropriate than RKFEM considering the oscillations presented.

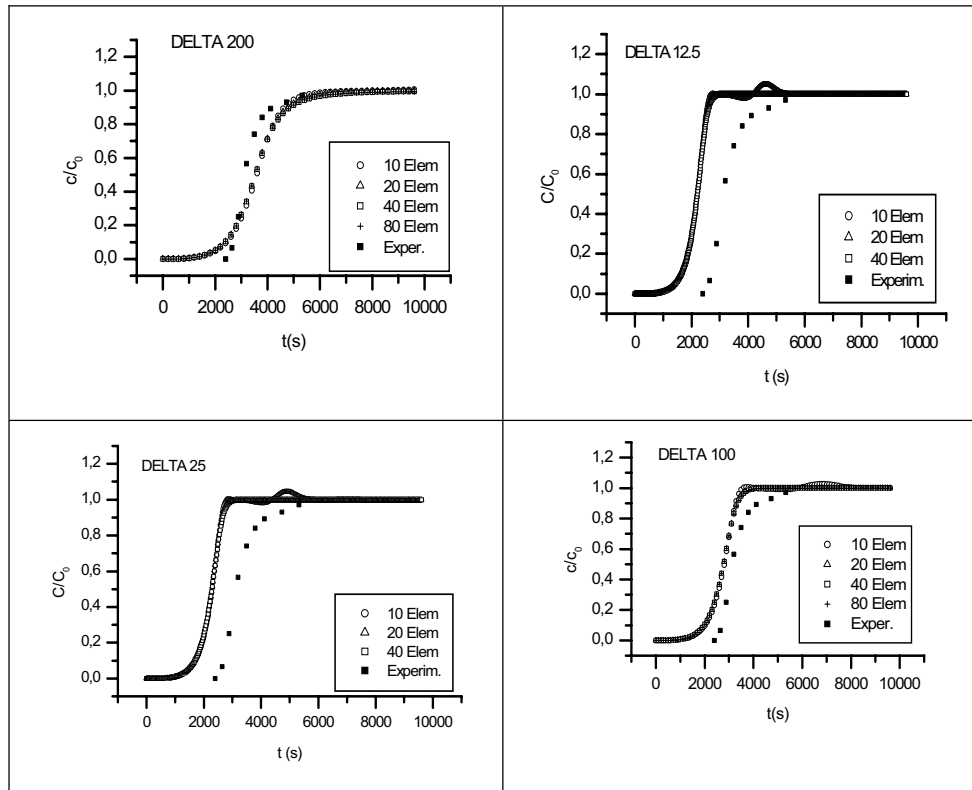


Figure 1: Breakthrough curve using CNFEM for $\Delta t = 200s, 12.5s, 25s$ and $100s$.

5. Conclusion

In this work, transformations and simplifications for the model of fixed-bed adsorption were proposed and it was shown that they did not change the response of the model and improved the numerical solution. The substitution of different isotherms showed adequate results. However, the involved parameters must be evaluated through empirical correlation available in the literature. Also, the FEM shows great advantages from the computational point of view, allowing the use of more refined Finite Elements meshes, and it has, also, enough conditions to support studies on binary or multi-components adsorption.

6. References

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