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Finite Element Method applied to a monocomponent liquid adsorption model with non-linear isotherm

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ABSTRACT

In this article the resolution and numeric results of the liquid adsorption problem in fixed-bed are shown. They were obtained through two numeric models, both using the Finite Elements Method (FEM) on space discretization and for time domain one used the Crank-Nicolson Method (CNFEM) and the other used the 4th Order Runge-Kutta Method (RKFEM). The mathematical model treated in this paper is uni-dimensional, composed by partial differential equations that describe the diffusive-convective transport. The adsorption equilibrium is described by Langmuir's non-linear isotherm. With this approach it was possible to study some of the unavoidable errors from any numeric solution. The methods implementation was done with MAPLE VI software, and the results obtained were qualitatively analysed and compared with experimental data.

1. INTRODUCTION

The application of Finite Elements Methods (FEM) on a great variety of complex problems has been studied by many sciences at the present. As examples, the geotechnical [1] and environmental engineering [7, 8, 9] studies of ground solutes transport, and the gases adsorption calculation done by chemical engineers [3].

In this work the FEM was applied to allow space discretization, considering a specific mono-component liquid adsorption model as referred in the papers of Buso et al [3] and Scheer [11]. For time discretization it was used the Crank-Nicolson Method (CNFEM) or the 4th Order Runge-Kutta Method (RKFEM).

Adsorption is the process where a selective concentration of one or more components of a gas as well as liquid are adsorbed on the surface of a micro porous solid. The mathematical equation that describes the adsorption equilibrium is the Langmuir's equation, where fluid concentration and adsorbate concentration are related [13].

With the recent developments on numeric computation and the need of more effectiveness simulation techniques, powerful softwares of dynamic chemical processes simulation have been designed mainly to

distillation process in petrochemical industry, some others concerns absorption and extraction, but an important process as the adsorption remains in second plan.

This work proposes the use of FEM on adsorption problems. The developed mathematical models were implemented with MAPLE VI software, and the results obtained were qualitatively analysed and compared with experimental data. The mathematical model, the FEM formulation and the CNFEM and RKFEM formulation are shown on section 2. Section 3 shows the results and on section 4 the discussion and some final comments are presented.

2. MATHEMATICAL MODEL

The diffusion on porous was the mathematical model used for the adsorption, where two mass transfer process are considered:

- the external mass transfer from the bulk liquid phase to the solid surface;
- the internal diffusion inside the particle's porous.

The liquid adsorption problem is described by mathematical model given by the following differential equations [3,11]:

$$e_e \frac{\partial c_e}{\partial t} + v\frac{\partial c_e}{\partial z} - D_L e_e \frac{\partial^2 c_e}{\partial z^2} = -K_L \frac{3}{R_p}\left(c_e - c_p\right)\left(1 - e_e\right) \tag{1}$$

$$e_i \frac{\partial c_p}{\partial t} = K_L \frac{3}{Rp}\left(c_e - c_p\right) - r_s\left(1 - e_i\right)\frac{\partial q}{\partial t} \tag{2}$$

$$\frac{\partial q}{\partial t} = \frac{aq_m}{\left(1 + ac_p\right)^2}\frac{\partial c_p}{\partial t} \tag{3}$$

Considering these initial and boundary conditions:

$$c_e(0,t) = c_e^F \qquad \frac{\partial c_e}{\partial z}(L,t) = 0 \qquad c_e(z,0) = 0 \qquad c_p(z,0) = 0 \qquad q(z,0) = 0 \tag{4}$$

where c_e is the concentration in the external liquid phase, c_p is the concentration of the liquid solution in the pore of the adsorbent particle, t is time and z is the vertical space coordinate.

Equation (3) is given by Langmuir's non-linear isotherm

$$q = \frac{aq_m c_p}{1 + ac_p} \tag{5}$$

where q is the adsorbate concentration, q_m is the maximum adsorbate concentration in the adsorbent, and a is a constant.

For variational form, considering weighted residuals, the equation (1) is written as: Find $C_e(z,t)$ such as

$$\int_0^L \left[\frac{\partial c_e}{\partial t} h + \alpha \frac{\partial c_e}{\partial z} h + \beta (c_e - c_p) h \right] dz + \int_0^L D_l \frac{\partial c_e}{\partial z} \frac{\partial h}{\partial z} = 0 \quad \forall h \tag{6}$$

where the function h is defined by the conditions on (4) as $h(0,t)=0$ [2].

The constants were grouped as follows:

$$\alpha = v / \varepsilon_e \qquad \beta = K_L \frac{3}{R_p} \left(\frac{1-\varepsilon_e}{\varepsilon_e} \right) \tag{7}$$

2.1. Numeric Models

The FEM has been under evaluation together with some integration techniques used to solve problems on time domain. Some examples can be found on a variety of problems involving hyperbolic and/or parabolic equations with studies and discussions about parameters variations [4, 7, 8, 9,12].

In the model presented, the FEM was applied to equation (1) and will be demonstrated in the next sections. Equations (2) and (3) were modified to adapt to the CNFEM and RKFEM methods, resulting in the time dependent non-linear differential equation:

$$\frac{\partial c_p}{\partial t} = \frac{\sigma (1 + acp)^2 (C_e - c_p)}{\left[(1 + ac_p)^2 + \Phi \right]} \tag{8}$$

onde

$$\sigma = \frac{3K_L}{\varepsilon_i R_p} \qquad \text{and} \qquad \Phi = \rho_s a q_m \frac{(1-\varepsilon_i)}{\varepsilon_i} \tag{9}$$

2.2. The Finite Elements Method applied to the adsortion column

The approximated solutions for equation (1) in its variational formulation, given by equation (6), are then built in the finite dimensional subspace of admissible functions, which satisfy the homogeneous boundaries conditions and are smooth enough to well define the integrals in a variational problem, also allowing the first derivatives to become square-integrable.

A partition is introduced in the (0,L) interval resulting in n sub-intervals, where one Finite Element involving two nods, i and j, is built to solve this problem by using piecewise linear functions for the interpolation inside the k element.

The following interpolations are proposed for $c_e(z,t)$ concentrations and for $h(z,T)$ "virtual concentrations":

$$c_e(z,t) = \sum_{j=1}^{n} N_j(z) C_e^j(t) \qquad h(z,t) = \sum_{i=1}^{n} N_i(z) H_i(t) \tag{10}$$

where

- n is the number of elements at the t moment;

- $c_e(z,t)$ are scalar functions obtained from the solution of a system of ordinary differential equations (1) and (4), with c_e unknown functions;
- C_e^i, H_i and N_i (z) are bulk phase concentration vector, "virtual concentrations" and constituted interpolation operator components, respectively. Replacing this relations into (6):

$$\sum_{i=1}^{n}\left\{\sum_{j=1}^{n}\left\{\int_k N_j N_i \frac{\partial C_e^j}{\partial t}dz+\left(\int_k \alpha \frac{\partial N_j}{\partial z}N_i dz+\int_k D_l \frac{N_j}{\partial z}\frac{\partial N_i}{\partial z}dz+\int_k \beta N_j N_i dz\right)C_e^j\right\}-\right.$$

$$\left.-\int_k \beta c_p N_i dz\right\}H_i = 0 \quad \forall H_i \tag{11}$$

as equality must be satisfied for every H_i component, then:

$$\sum_{i=1}^{n}\left\{\sum_{j=1}^{n}\left\{\int_k N_j N_i \frac{\partial C_e^j}{\partial t}dz+\left(\int_k\left(\alpha \frac{\partial N_j}{\partial z}N_i + D_L \frac{\partial N_j}{\partial z}\frac{\partial N_i}{\partial z}+\beta N_j N_i\right)dz\right)C_e^j\right\}-\right.$$

$$\left.-\int_k \beta c_p N_i dz\right\} = 0 \tag{12}$$

for $i = 1,...,n$.
Considering

$$m_{ij} = \int_k N_j N_i dz \qquad k_{ij} = \int_k\left(\alpha \frac{\partial N_j}{\partial z}N_i + D_L \frac{\partial N_j}{\partial z}\frac{\partial N_i}{\partial z}+\beta N_j N_i\right)dz \qquad f_i = \beta\int_k c_p N_i dz \tag{13}$$

equation (12) can be written as

$$\sum_{j=1}^{n}\left\{m_{ij}\frac{\partial C_e^j}{\partial t}+k_{ij}C_e^j\right\}^j - f_i = 0 \quad \text{para} \quad i = 1,..,n \tag{14}$$

or

$$M^k \frac{\partial C_e^k}{\partial t}+K^k C_e^k - F^k = 0 \tag{15}$$

where M^k, K^k, C_e^k and F^k are matrix and vectors formed by the components m_{ij}, k_{ij} and f_i, 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, as follows:

$$\sum_{k=1}^{nel} \boldsymbol{L}_k^T \left(\boldsymbol{M}^k \frac{\partial \boldsymbol{C}_e^k}{\partial \boldsymbol{t}} + \boldsymbol{K}^k \boldsymbol{C}_e^k - \boldsymbol{Y}^k \right) \boldsymbol{L}_k = 0 \tag{16}$$

where *nel* is the number of elements.

From (16) is obtained the global system of differential equations:

$$M \frac{\partial C_e}{\partial t} + KC_e - F = 0 \tag{17}$$

2.3. Formulation using CNFEM and RKFEM methods

Many integration techniques can be used to solve time domain problems. For the CNFEM application on this model, expression (17) is assumed as:

$$[A]\{C_e\}^{t+\Delta t} = [B] \tag{18}$$

where

$$[A] = \left[\frac{2}{\Delta t} M + K \right] \qquad \text{e} \qquad [B] = \left[\frac{2}{\Delta t} M - K \right] \{C_e\}^t + 2[F] \tag{19}$$

In this study, the matrix are calculated once for each *t* moment, obtaining $C_e(t)$. Then c_p is calculated with CNFEM in equations (8) and (9) for each *t* moment. After that, the calculation follows an iterative process. For the RKFEM application, the same process was used, but the matrix were calculated at each RKFEM phase.

3. RESULTS

The study of packed bed adsorption columns is based on the analyse of time X bulk phase concentration curves, which are influenced by column geometry, operational conditions and equilibrium data. This curves, referred as Breakthrough Curves, result from the concentration output monitoring of a fluid that passes through a packed bed. After some time the bed becomes saturated, and the output concentration approaches the input concentration. The area behind the breakthrough curve represents the quantity of adsorbate retained in the column. This corresponds to a point on the equilibrium isotherm [11].

The numeric results presented in this section are based on the comparison with Santacesaria experimental results [10] for the m-xylene component. The following parameters were considered for this specific problem:

$$T = 9600s, L = 40cm, D_L = 1.29E-2, \boldsymbol{e}_e = 0.42, \boldsymbol{e}_i = 0.2, R_p = 6.5E-2, v = 1.98E-2,$$
$$\boldsymbol{r} = 1.4E3, a = 4.2L/mol, K_L = 1.09cm/s, q_m = 1.75E-3, c_e^f = 78E-2. \tag{20}$$

The results generated by CNFEM are shown in Figure 1, as those by RKFEM are in Figure 2. Each graphic represents the space discretization refinement for a stipulated time increment. For the CNFEM, time increments of 200, 100, 50, 25 and 12.5 seconds were studied and space refinements were obtained for 10, 20, 40 and 80 elements. For the 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.

It can be noted that time increments of 200s and 100s for CNFEM and 100s for RKFEM are those that better fit with experimental data. According to Ferziger and Péric [5], special care must be taken when interpreting these results, considering that different kinds of mistakes can be hidden by results that appear to converge to experimental data. Although, with mesh refinement, the curves tend to displacement from experimental data, but all of them converge to the same solution, for both methods.

This fact, however, can also indicate a modelling error due to the chosen parameters. It can also be noted that the oscillations tend to disappear while mesh refinement is improved, what means that this method can be adjusted depending on the refinements, allowing further studies on the parameters set.

In the last graphic of each figure it is presented the mesh simultaneous refinement, aiming to detect possible numeric errors.

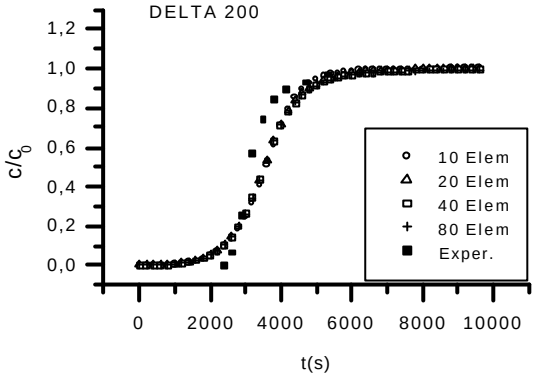
4. DISCUSSION AND FINAL COMMENTS

At first sight, the model manipulation was adequate to methods application, considering some simplifications as the boundaries conditions. The numeric model, still under study, showed good accordance with experimental data, but it has some factors that must be better analysed. In this case, the concepts of Ferziger and Péric [5] have been used as a tool for results analyses, knowing that errors are unavoidable in numeric solution.

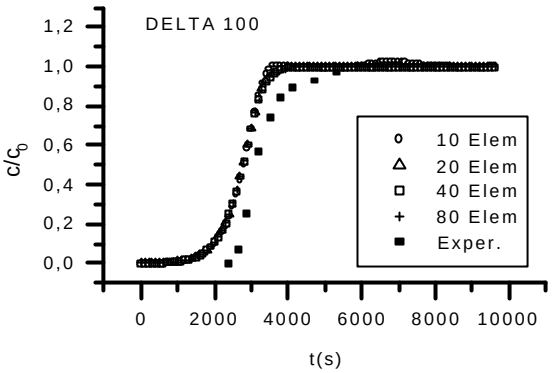
With meshes refinement it is believed that errors were minimised, as good convergence was obtained. Both models showed the same behaviour, but trying to reach an acceptable error level for the problem, the analyses indicate that CNFEM was more appropriate than RKFEM considering the oscillations presented. When refinement is used on both variables, the results are free from oscillations and there is no need to use others artefacts commonly utilised in this kind of analyses. The curve displacement, comparing with experimental data, must be better studied.

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.

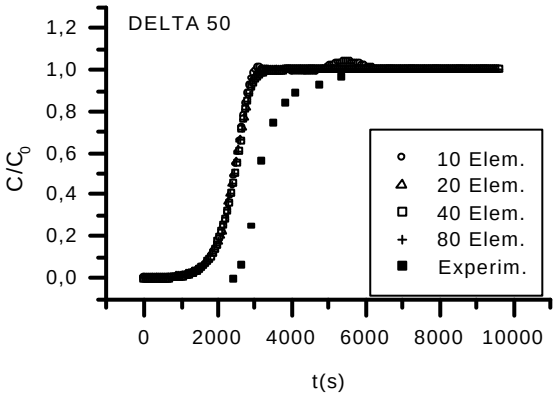
a)


DELTA 200
c/c0
1,2
1,0
0,8
0,6
0,4
0,2
0,0
0
2000
4000
6000
8000
10000
t(s)
10 Elem
20 Elem
40 Elem
80 Elem
Exper.

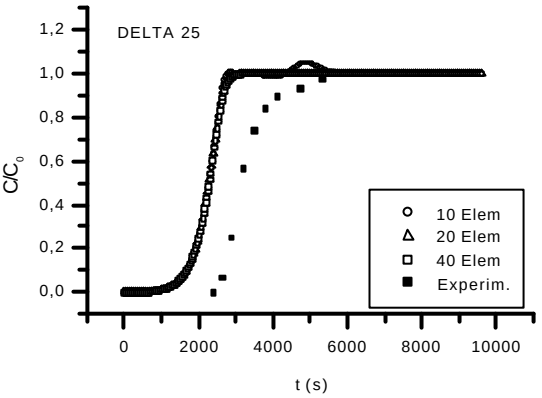
b)


DELTA 100
c/c0
1,2
1,0
0,8
0,6
0,4
0,2
0,0
0
2000
4000
6000
8000
10000
t(s)
10 Elem
20 Elem
40 Elem
80 Elem
Exper.

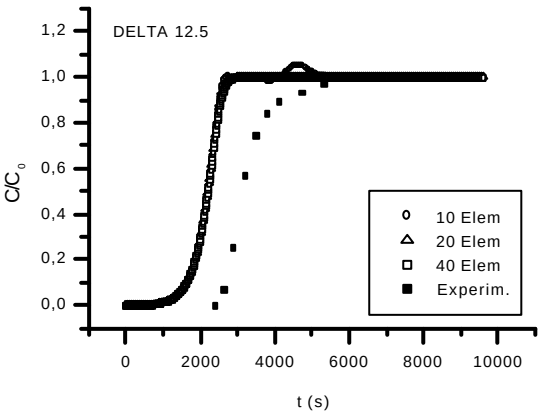
c)


DELTA 50
C/C0
1,2
1,0
0,8
0,6
0,4
0,2
0,0
0
2000
4000
6000
8000
10000
t(s)
10 Elem.
20 Elem.
40 Elem.
80 Elem.
Experim.

d)


DELTA 25
C/C0
1,2
1,0
0,8
0,6
0,4
0,2
0,0
0
2000
4000
6000
8000
10000
t (s)
10 Elem
20 Elem
40 Elem
Experim.

d)


DELTA 12.5
C/C0
1,2
1,0
0,8
0,6
0,4
0,2
0,0
0
2000
4000
6000
8000
10000
t (s)
10 Elem
20 Elem
40 Elem
Experim.

e)

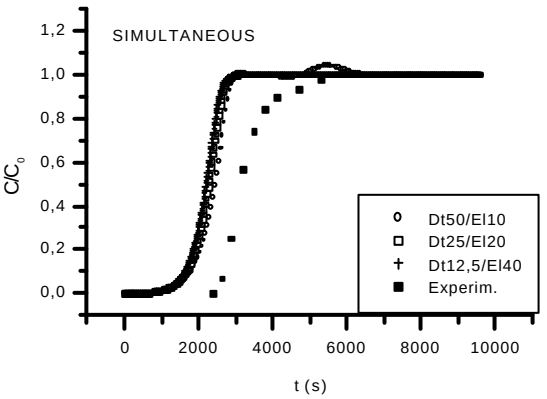

SIMULTANEOUS
C/C0
1,2
1,0
0,8
0,6
0,4
0,2
0,0
0
2000
4000
6000
8000
10000
t (s)
Dt50/El10
Dt25/El20
Dt12,5/El40
Experim.

Figure 1: Breakthrough curve simulated by CNFEM for a) Ät = 200s, b) Ät = 100s, c) Ät = 50s, d) Ät = 25s, e) Ät = 12.5s and f) Simultaneous refinement (space and time).

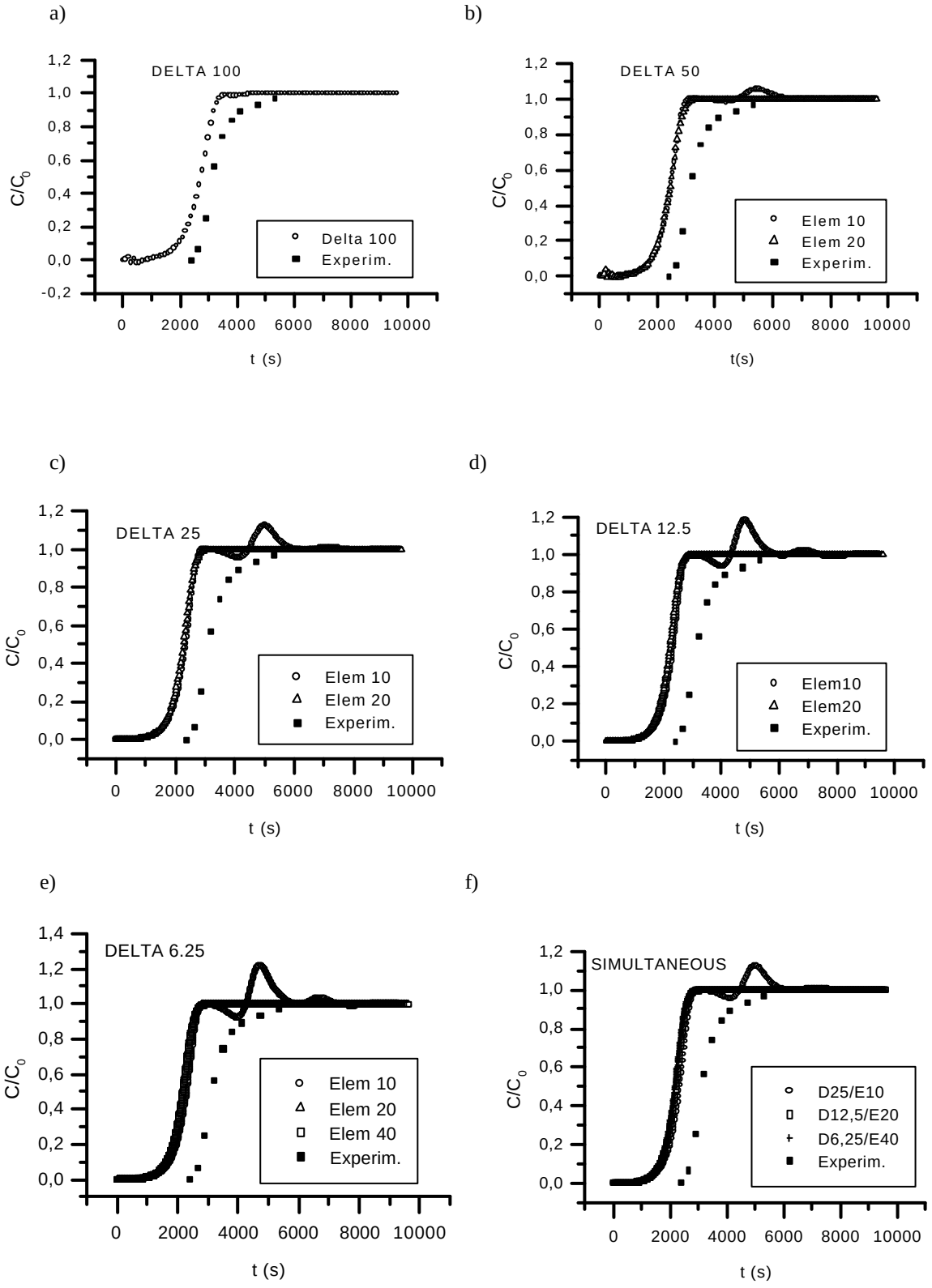


Figure 2: Breaktrhough Curve simulated by RKFEM for a) Ät = 100s, b) Ät = 50s, c) Ät = 25s, d) Ät = 12.5s, e) Ät = 6.25s and f) Simultaneous refinement (space and time).

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