SIMULTANEOUS DETERMINATION OF DISPERSION AND NONLINEAR ADSORPTION PARAMETERS BY USING NUMERICAL MODELS AND OPTIMIZATION TECHNIQUES

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RESUMEN

La determinaciòn simultànea de los parâmetros de dispersiòn y adsorciòn no lineal se realiza en forma automàtica. Es decir, se ajustan los perfiles de concentraciòn medidos en el laboratorio con los obtenidos numericamente. El ajuste se realiza aplicando tècnicas de optimizaciòn multivariable para minimizar las diferencias entre los resultados numèrico y experimental. La ecuaciòn diferencial se resuelve numericamente por diferencias finitas aplicando el mètodo de Crank-Nicolson.

Los resultados muestran que cuando se optimizan los tres parâmetros simultaneamente, el vector soluciòn hallado no es ùnico y depende del modelo de adsorciòn. Esto implica que los parâmetros estân correlacionados.

ABSTRACT

The simultaneous determination of the dispersion and nonlinear adsorption (Freundlich or Langmuir) parameters is obtained automatically by matching results of numerical models with experimental data from a laboratory displacement test.This matching is performed by applying multivariable optimization techniques to minimize the differences between numerical and experimental results. Numerical solutions are obtained by solving the convection-dispersion-nonlinear adsorption equation by finite differences using the Crank-Nicolson method with iterations to account for nonlinearities.

These results show that whenever the three parameters are simultaneously determined, the vector solution is not unique and it depends on the adsorption model. Therefore, the parameters are correlated.

INTRODUCTION

The determination of the dispersion and adsorption parameters for flow throughout porous media is of interest in the engineering design of many processes. Among them: adsorption beds, ion exchange columns and chromatography in chemical engineering; enhanced oil recovery processes in reservoir engineering; and solute transport in the soil, in soil physics, could be mentioned.

The movement of solute in porous media is governed by the convection-dispersion-adsorption partial differential equation.

Analytical solutions for one-dimension and various boundary and initial conditions have been found for the convection-dispersion equation combined with a linear equilibrium adsorption (Lapidus and Amundson [1], Bastian and Lapidus [2], Brenner [3]). However, when considering nonlinear adsorption, numerical methods ought to be applied. The two most popular nonlinear adsorption models are Freundlich and Langmuir equations. The introduction of any of these two models in the convection-dispersion-adsorption equation, results in a nonlinear parabolic differential equation . Numerical solutions have been obtained by finite differences (Gupta and Greenkorn [4], Gabbanelli et al. [5], Smith and Keller [6], Satter et al.[7], Carpano et al. [8]), by orthogonal collocation (Coppola and Levan [9]) and by finite elements (Vossoughi et al.[10]).

This paper deals with the inverse problem: determination of the dispersion and nonlinear adsorption parameters of the partial differential equation, by matching the results of the numerical model with the experimental measurements.

These experimental measurements are usually: dimensionless solute concentration versus dimensionless time at outlet. Performing a displacement test in the laboratory, and introducing a change in the solute concentration at inlet, the breakthrough curve is obtained.

The experimental breakthrough curve can be fitted to the numerical solution using a least squares method. In order to find the best match, three parameters are varied:the dispersion coefficient and two adsorption parameters.

Gupta and Greenkorn[11] assumed the principle of superposition to determine the three parameters separately. Thus, the dispersion coefficient was estimated by analyzing the breakthrough curve for a non-adsorbing species. One of the adsorption parameters, of the Freundlich isotherm, was determined by static adsorption experiments. The other was found from a generalized nonlinear regression. Gabbanelli et al. [5] applied a similar procedure: the two Langmuir adsorption parameters were estimated by static experiments and the dispersion coefficient was found when minimizing the objective function (the sum of the square of the differences between experimental and numerical concentrations). This minimization was done by applying the Fibonacci technique [12].

The history-match process was also applied to find the two parameters of the Langmuir equilibrium isotherm and the dispersion coefficient by Vossoughi [10]. In his proposal one parameter was

changed at a time, and the lowest value of the objective function was determined for that parameter at fixed values of the others.

Cameron and Klute [13], worked out a different convection-dispersion-adsorption equation which represents linear equilibrium and a kinetic adsorption model; and has analytical solution. Consequently, he found the three parameters of the analytical solution by applying the Powell [14] optimization technique to minimize the differences between the predicted and the experimentally observed breakthrough curves.

It is worth mentioning that automated matching has been used for a different model: the convection-dispersion-capacitance model of Deans [15]. This model has analytical solution in Laplace space. For this reason, Baker [16] proposed the transformation of experimental data to the frequency domain, and an algebraic curve fitting procedure in the frequency domain. Unfortunately, Batycky et al. [17] studying simulation of miscible displacement in carbonate-cores, concluded that the curve fitting in the Laplace-transform domain and in the real time domain is not equivalent. They found the three parameters of the convection-dispersion-capacitance model by using an implicit finite-difference simulator and a sequential search in the real time domain to minimize the error of this matching.

In this work the convection-dispersion-non linear adsorption differential equation is solved. Two adsorption equilibrium models, the Freundlich and Langmuir ones, are considered. The numerical solution is obtained by using a Crank-Nicolson implicit scheme with an iterative procedure to take into account the nonlinearities. The automated matching is performed by defining an objective function which is the sum of the squares of the residuals. Residual is the difference between the experimentally observed and the numerically calculated concentration. The objective function is minimized by varying the three parameters simultaneously, with two different optimization techniques: Levenberg-Marquardt's [18] and Complex of Box's[12].

CONVECTION-DISPERSION-NONLINEAR ADSORPTION MODEL

The transport equation characterizing convection, dispersion and adsorption of a solute flowing through a porous medium can be written as,

$$\frac{\partial C}{\partial t} + \frac{\partial C_r}{\partial t} = K \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \qquad (1)$$

The most important assumptions in eq. (1) are:

1- The porous medium is homogeneous with constant cross section and porosity.
2- The flow is isothermal and one-dimensional.
3- The intersticial velocity, v - obtained dividing Darcy velocity by

porosity-, is constant.
4- The dispersion of the solute occurs in the longitudinal direction. The dispersion coefficent, K, is independent from concentration and it is constant at a fixed velocity.
5- There is no chemical reaction between the injected solution and the rock or the fluid in-situ.

Considering a semi-infinite porous medium [19], boundary conditions to solve eq. (1) are :

$$C(0,t) = C_o \qquad t > 0$$
$$C(x,t) \to 0 \quad \text{if } x \to \infty \qquad t > 0. \tag{2}$$

Initial condition is

$$C(x,0) = 0. \tag{3}$$

Defining dimensionless variables

$$C_d = \frac{C}{C_o} \qquad x_d = \frac{x}{L} \qquad t_d = \frac{v\,t}{L} \qquad C_{rd} = \frac{C_r}{C_o} \tag{4}$$

and using the Peclet number as dimensionless parameter

$$Pe = \frac{v\,L}{K} \tag{5}$$

The eqs. (1), (2) and (3) are rewritten as,

$$\frac{\partial C_d}{\partial t_d} + \frac{\partial C_{rd}}{\partial t_d} = \frac{1}{Pe}\,\frac{\partial^2 C_d}{\partial x_d^2} - \frac{\partial C_d}{\partial x_d} \tag{6}$$

$$C_d(0,t_d) = 1 \qquad t_d > 0$$
$$C_d(x_d,t_d) \to 0 \quad \text{if } x_d \to \infty \qquad t_d > 0 \tag{7}$$

The term $\partial C_{rd} / \partial t_d$ in eq. (1) represents the adsorption of solute onto the rock. It is obtained by taking the derivative of the appropriate adsorption isotherm as,

$$k_1\, \partial C_d / \partial t_d \qquad \text{Linear} \tag{8}$$
$$k_2\, n\, C_d^{(n-1)}\, \partial C_d / \partial t_d \qquad \text{Freundlich} \tag{9}$$
$$k_3\, (1 + bC_d)^{-2}\, \partial C_d / \partial t_d \qquad \text{Langmuir} \tag{10}$$

NUMERICAL SOLUTION

Transport equation (6) is numerically solved by finite differences applying the Crank-Nicolson method and an iterative scheme to take into account the nonlinearities. Truncation error and stability of the numerical scheme have been previously analyzed [5], [8].

Dimensionless space and time increments which are equal to 0.01 yield a good numerical behaviour [8]. Semi-infinite boundary condition is simulated increasing the number of grid points as time increases[20].

OPTIMIZATION METHODS

The convection-dispersion-nonlinear adsorption equation has three characteristic parameters: Peclet number and two adsorption parameters.

The two adsorption parameters could be determined from static adsorption experimental tests. The dispersion coefficient could be estimated from correlations [21]. These correlations, in turn, are based on analytical solutions of the convection-dispersion equation.

Therefore, it is desirable to evaluate the three parameters simultaneously from dynamic tests - i.e. displacement or flooding laboratory tests -. From these tests solute concentration as a function of time is usually measured at outlet. On the other hand, the numerical solution of eq. (6) also provides solute concentration as a function of time. Therefore, an objective function ,FO, which is the sum of the squares of the residuals can be defined. Residuals are the differences between numerical and experimental concentrations.

Considering the Langmuir model,

$$FO\ (Pe,k_3,b) = \sum_{i=1}^{M} [C_d|_{exp}(t_i) - C_d|_{num}(t_i,Pe,k_3,b)]^2 \qquad (11)$$

for Freundlich adsorption model k_3 and b are both replaced for k_2 and n,respectively. For linear adsorption k_3 and b, both are replaced just by one parameter k_1.

The vector of the three parameters which minimizes eq. (11) is found by applying two different optimization techniques: Complex of Box's [12] and Levenberg-Marquardt's [18], in order to compare their results.

Complex of Box is an alternative version of the simplex method which searches for the minimun of a n-variable objective function with constraints. The search is stopped when for some consecutive function evaluations, the mean change of the parameters differs less than a prescribed tolerance, called COTA, here.

Levenberg-Marquardt's method is a somewhat more refined technique which combined the best features of the Taylor series method and the gradient methods,ones. The convergence criterion is satisfied if,on two successive iterations, the parameter estimates agree component by component to NSIG digits.

Penalty function [18] is added to this technique in order to consider the physical constraint of the vector of the parameters.

RESULTS AND DISCUSSION

The proposed model was tested against measurements from flooding experiments in the laboratory. Three cases are shown and analyzed: aqueous solution of NaI tagged with I^{131}/brine displacement through a sandpack; aqueous solution of two percent NaCl tagged with tritiated water/brine displacement through Berea rock and solution of commercial polymer 454 in two-percent NaCl/brine displacement through Berea rock.

Experimental floods have been previously reported, therefore, only a brief description of the tests is outlined here. On the contrary, results of the automated matching are presented in detail.

Aqueous solution of NaI tagged with I^{131}/brine displacement.

Grattoni et al. [22], performed displacement tests on a sandpack impurified by clay. Initially, the sandpack was filled with water. At the inlet boundary, a constant concentration solution of INa tagged with I^{131} is injected continuously at a constant flow rate. As the solution is displaced forward due to the pressure gradient, the radioactive salt is dispersed and, it is also adsorbed onto the surface of the porous media.

During the run, the activity coming from the tracer is measured as a function of distance from inlet and as a function of time. Normalized activity profiles are represented as dimensionless concentration as a function of time at outlet in Fig. 1. Porous media and fluid characteristics can be seen in Table 1.

An automated matching is performed on experimental data at outlet. Peclet number and the two parameters of Langmuir's model are found applying two optimization techniques in parallel: Complex of Box's (COTA=0.001) and Levenberg-Marquardt's (NSIG=3). The values obtained by these two methods coincide and can be seen in Table 2-Case A. Furthermore, Peclet number and the two parameters of the Freundlich model are found applying the same two methods. Results can be seen in Table 2-Case B. It is startling to notice that the Peclet number obtained when adsorption is ruled by the Langmuir model is more than five times bigger than the one calculated with the Freundlich model. Therefore, adsorption isotherms shown in Fig. 2, also differ. For Case A, the curve is concave upwards. For case B, it is convex upwards.

In order to analize this nonuniqueness, Levenberg-Marquardt's method is applied with the two adsorption models as follows. In Case C, Pe =5.53 is fixed (value obtained in case B) and the two parameters of the Langmuir model are varied. Results of Table 2-Case C show that the adjustment is good though the objective function value is greater than before (error is increased). On the other hand, in Case D, Pe =29.7 is fixed (value obtained in case A for the Langmuir model), and the two parameters of the Freundlich model are varied. Results of Table 2-Case D show a worse match, because the objective function value is nearly five times greater than in Case A or in Case B. Finally, a linear model is tried (Table 2-Case E). It gives an intermediate value of the objective function. The values chosen for the parameters, to begin the

search. are:

Langmuir	Pe = 12.1	k_3 = 1.25	b = -0.175
Freundlich	Pe = 12.1	k_2 = 1.58	n = 1.12
Linear	Pe = 15.0	k_1 = 0.736	

Adsorption isotherms taken as starting values for the Langmuir and the Freundlich models are similar, both are concave upwards.

Adsorption isotherms are drawn for cases A, B, C, D and E in Fig. 2. Curves corresponding to cases B and C are both convex upwards.

In Fig. 3, experimental dimensionless concentration as a function of distance from inlet, and time are represented as points for the same data set of Table 1. Numerical results for cases A, and B are shown as continuous curves.

The matching was performed on experimental data at outlet . There, the cases A, B, C, D and E have an acceptable adjustment with experimental data. However, differences are appreciable for points inside the porous media. Moreover, the numerical curves are closer to each other than with experimental measurements. For that reason, a new global error, E_{exp} , is estimated,

$$E_{exp} = \sum_{i=1}^{M} \sum_{j=1}^{N} [C_d|_{exp}(t_{di},x_{dj}) - C_d|_{num}(t_{di},x_{dj},Pe,k_3,b)]^2, \qquad (12)$$

Let us notice that eq. (12) is not an objective function to be minimized. It is only the summation of the square of the residuals, for measurements in time (M) and space (N).

Global errors, E_{exp} , and mean errors with respect to each measurement, $\sqrt{(E_{exp}/(N+M))}$ can be seen in Table 3. Errors are very big and similar for all cases. However, case A shows the smallest error. Therefore a new error of other numerical solutions (cases B, C, D and E) with respect to case A, E_A , is introduced,

$$E_A = \sum_{i=1}^{M} \sum_{j=1}^{N} [C_d|_A(t_{di},x_{dj}) - C_d|_{num}(t_d,x_{dj},Pe,k_3,b)]^2 \qquad (13)$$

where $C_{d\,A}$ are the numerical dimensionless concentrations corresponding to case A. It is evident that $E_A < E_{exp}$, and the models do not reproduce the experimental test. Discrepancies could arise from several sources: the packing could be inhomogeneous, permeability and porosity could vary with space, they could also vary with time if the fine sand grains are carried forward by the fluid. For this reason, the intersticial velocity and the dispersion coefficient would be neither constant in space nor in time. In this case eq. (8) will not rule the convection-dispersion-adsorption phenomenon. Thus, eq. (11), could be adjusted with experimental data at outlet but it fails to match experimental measuresents inside and along the sandpack.

Uncertainty in parameter determination

The uncertainty in the determination of the parameters is estimated following Batycky et al. [17]. This is done by evaluating the sensitivity of the objective function value to changes in the parameter values around the optimum. Here, the change in the optimized value of a parameter necessary to increase the objecive function value by 50% is taken as the uncertainty in determination of that parameter.

In order to obtain the uncertainty in one parameter, minimization of the objective function is carried out by varying that parameter, while the other two remain fixed. Minimization is performed by applying Fibonacci's[12] optimization technique, which is appropriate for variation of one parameter at a time.

Uncertainty values thus calculated are:

Langmuir model (Case A)
Pe = 29.7 ± 2.5 k_3 = 0.736 ±0.0013 b = 0.540±0.015

Freundlich model (Case B)
Pe = 5.53 ± 0.31 k_2 = 1.61 ± 0.03 n = 0.710±0.037

Aqueous solution of NaCl tagged with tritiated water/brine displacement.

Szabo [23] studied polymer retention in porous media. Two of his experimental curves are simulated here. The first one is the dimensionless concentration of tritiated water as a function of dimensionless time (Fig. 4). The curve was obtained displacing brine by 2-percent NaCl brine tagged with tritiated water. The displacement was performed on a Berea Rock core, the characteristics of which can be seen in Table 1. After two pore volumes of tritiated water were injected, the core was flushed with three pore volumes of regular brine. Then a 600 ppm solution of commercial Polymer 454 in two-percent NaCl water was injected. The polymer breakthrough curve was determined by viscosity measurements. It is shown in Fig. 5 and it will be analyzed in the next section.

The numerical model described here is matched with experimental measurements shown in Fig. 4. The automated matching is performed by applying Complex of Box's and Levenberg-Marquardt's methods and varying simultaneously the three parameters corresponding to dispersion and either the Langmuir or the Freundlich models. Optimal parameters and objective function values are shown in Table 4. From that table, it is evident that the adsorption is practically linear . Consequently, Levenberg-Marquardt's optimization technique was applied again, but considering linear adsorption and varying Peclet number and the linear adsorption parameter k_1 . The matching was done using the numerical model and the analytical solution. These results are also shown in Table 4, and drawn in Fig. 4. Finally, Peclet number was calculated by the analytical-graphical method proposed by Brigham [24]

$$Pe = \left(\frac{3.625}{U_{90}-U_{10}} \right)^{-2} \qquad \text{where} \qquad U = \frac{t_d - 1}{(t_d)^{0.5}} \cdot \qquad (14)$$

The function U is plotted versus the percent of displacing fluid on arithmetic probability paper, U_{90} and U_{10} correspohd to 90 and 10 percent displacing fluid respectively. Applying this procedure,

$Pe = 71.1$

Conclusions from Table 4 and Fig. 4 are: adsorption is linear, parameter values obtained by different methods agree reasonably well, objective function values and mean errors are small.

Uncertainty values for the parameters are estimated by the method described above. They are, $Pe = 72.2 \pm 3.9$, $k_1 = 0.0760 \pm 0.0050$.

Aqueous solution of Polymer 454/brine displacement

In Fig. 5 Szabo's experimental measurements of dimensionless polymer concentration as a function of dimensionless time at outlet are shown. These measurements have been taken from a displacement of regular brine by a 600 ppm solution of commercial Polymer 454 in two-percent NaCl-water, through a Berea rock ,the characteristics of which can be seen in Table 1.

"Automated" matching is performed on the experimental data. Peclet number and the adsorption parameters corresponding to the Langmuir, the Freundlich or the linear models can be seen in Table 5.

Starting values of the parameters are:

Langmuir	Pe=187	k_3=0.186	b= -0.455
Freundlich	Pe=187	k_2=0.304	n= 1.24
Linear	Pe=150	k_1=1.00	

The results obtained by applying Levenberg-Marquardt's technique (NSIG = 3) are in total agreement with the results obtained by Complex of Box's (COTA = 0.001), thus only one set of results is shown in Table 5. Case A corresponds to Langmuir's model optimizing the three parameters simultaneously and case B to Freundlich's model. Objective function values are low and similar. Once again, Peclet number and adsorption isotherms differ. They are shown in Fig. 6, for case A the isotherm is concave upwards and for case B it is convex upwards.

Both adsorption models are again applied here so as to analyze the nonuniqueness; this time decreasing the degrees of freedom. In case C, Pe=44.5 is fixed at the optimum value for the Freundlich model (case B), and k_3 and n are varied. Objective function value duplicates. In case D, Pe =254 is fixed at the optimum value for case A, and k_2 and n are varied. Objective function value in this case increases nearly ten times. Adsorption isotherms are shown in Fig. 6 convex upwards for case C and downwards for case D. In case E, the matching is done with a linear adsorption model. The objective function value is also higher than in case A and B.

By examining Table 5, we conclude that the results of cases A and B are equivalent and they are the best.

In Fig. 5, dimensionless concentrations calculated for cases A, B and experimental points are shown.

Uncertainty values in parameter determination, calculated as before, are:

The Langmuir model (case A)
Pe = 254 ±49 k_3 = 0.172 ±0.004 b = 0.499 ±0.008
The Freundlich model (case B)
Pe = 44.5 ±2.6 k_3 = 0.346 ±0.006 n = 0.744 ±0.035

Stopping criteria

The final values of parameters obtained, by applying either Levenberg-Marquardt's or Complex of Box's algorithms, depend on the stopping criterion. The stopping criterion, in turn, influences the value of the objective function -the goodness of the match -.

In this paper, a mean residual error per measurement is defined as $\sqrt{(FO/M)}$. The search of the optimal parameters is continued while the mean residual error per measurement is bigger than the experimental error of dimensionless concentration. It is stopped when

$$\sqrt{(FO/M)} < \text{experimental error}$$

It is considered that the experimental error of the dimensionless concentration is around 0.01

In Table 6 the variation of the objective function value, the mean residual error per measurement and the optimal parameters with the Complex of Box's stopping criterion are shown. The objective function value reaches its minimum at FO= 0.00107, COTA = 0.005, and it remains constant for smaller values of COTA. The same behaviour is found for different sets of experimental data and for the Levenberg-Marquardt algorithm.

Influence of the initial values of the parameters

In order to analyze the nonuniqueness of the vector solution of the parameters, the initial values of the parameters are varied. The results are shown in Table 7, and they refer to the Langmuir adsorption isotherm (case A). Only one alternative solution - to the one already shown - is found. The solution has Pe = 29.5 which is closer to the one found in case B. The adsorption curve corresponding to k_3= 0.983 and b=1.84 is drawn in Fig. 8 (Case A). It is convex upwards like in case B, but the curvature is more evident. The objective function value is slightly smaller than in case A.

Therefore, the nonuniqueness of the solution is caused not only by a different adsorption model (Langmuir's, Freundlich's or linear). Here, two very good and different solutions are obtained for the Langmuir model just by changing the initial values of the parameters.

So as to lay aside numerical or optimization errors the following procedure was done. The numerical solution $C_d(t_d, x_d=1)$ obtained with the set of parameters for case A (Pe =254, k_3 = 0.172, b=- 0.499) is arbitrarily taken as experimental data. The Levenberg-Marquardt technique is applied with the initial values of Table 7. Identical

results are obtained, but with a more favourable objective function value. They are also shown in Table 7.

It is worth mentioninig that when traying different initial values with the Freundlich model, only one solution with an error ($\sqrt{FO/M}$) less than the experimental error is found. This is case B. Other solutions show a bigger error.

On the other hand, for the displacement of an aqueous solution of NaI tagged with I already described (Table 2, Fig. 1 and Fig. 2) an alternative set of final parameters is found. Starting with a non-realistic set of initial values: Pe=1.0, k_3=0.736, b=0.9; the following set of final values is encountered : Pe=3.22, k_3 =7.15 and b =3.3 . The objective function value, FO =0.138×10^{-2}, is small and similar to the one found in Table 2. However the final values k_2 and b give an adsorption isotherm with a marked and non-realistic curvature.

CONCLUSIONS

A method for matching a convection-dispersion-nonlinear adsorption model (either Langmuir's or Freundlich's) with experimental data is presented. The match is automatically done by applying optimization techniques to minimize the differences between numerical and experimental results. The minimization is accomplished by varying three characteristic parameters: Peclet number and adsorption parameters.

The conclusions are:

1- The results obtained with two different optimization techniques, Levenberg-Marquardt's and Complex of Box's, are identical.

2- For linear equilibrium adsorption, a unique set of two parameters (and k_1) is obtained.

3- For nonlinear equilibrium adsorption, if the three parameters are simultaneously obtained, the vector solution is not unique and depends on the adsorption model. If a given set of experimental data from laboratory displacements is well adjusted with Langmuir's adsorption model for a high Peclet number and an adsorption curve concave upwards, it can also be matched with Freundlich's adsorption model for a low Peclet number and an adsorption curve concave downwards. This kind of nonuniqueness occurs in every case.

4-One set of experimental data could be adjusted with Langmuir's adsorption model, but with two different vector solutions of the three parameters. One set of parameters consists of a relatively high Peclet number and an adsorption curve upwards. The other shows an extremely low Peclet number, and adsorption curve with pronounced concavity downwards; this seems physically non-realistic.

5-Another set of experimental data consists of concentration distributions as a function of distance from inlet and as a function of time. The outlet concentration profile is well reproduced with Peclet number and the adsorption parameters are obtained by automated matching However, the convection-dispersion-nonlinear adsorption equation using these parameters does not exhibit a good match with experimental concentration profiles along and inside the porous medium. One might infer that the intersticial velocity and the dispersion coefficient may be neither constant in space nor in time. In other words, the assumptions taken may not be realistic.

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NOTATION

C : concentration of solute, M/L.

C_d : dimensionless concentration of solute.

C_o : concentration of injected solute, M/L^3.

C_r : amount of solute adsorbed per unit of volume of fluid, M/L^3.

C_{rd} : dimensionless amount of solute adsorbed per unit of volume of fluid.

COTA : convergence criterion of Complex of Box method.

E_A : global error, defined by eq. (14).

E_{exp} : global error, defined by eq. (13).

FO : objective function to be minimized.

K : longitudinal dispersion coefficient, L^2/t.

k_1 : parameter for the linear adsorption model.

k_2, n : parameters for the Freundlich adsorption model.

k_3, b : parameters for the Langmuir adsorption model.

L : length of porous medium, L.

M : number of time data points.

N : number of space data points.

Pe : Peclet number, defined by eq. (5).

NSIG : convergence criterion of the Levenberg-Marquardt method.

t : time, t.

t_d : dimensionless time.

v : intersticial velocity, L/t.

x : distance from inlet, L.

x_d : dimensionless distance from inlet.

U : function of dimensionless time, defined by eq. (15).

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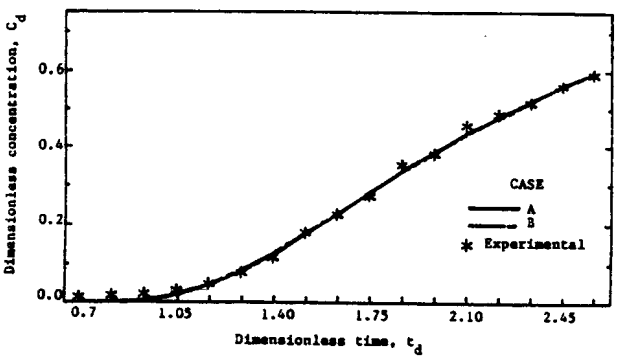

FIGURE 1 : Aqueous solution of INa tagged with I^{131} flooding. Dimensionless concentration as a function of dimensionless time at outlet. Comparison among experimental data and results estimated for different adsorption models (Freundlich's and Langmuir's). Levenberg-Marquardt's optimization method was used in the graphical representation (NSIG=3).

Porous media	Sand-quartz clay packing [22]	Berea natural core [23]	Berea natural core [23]
Particle diameter (mm)	0.044-0.42	------	------
Length (cm)	32.00	14.0	14.0
Diameter (cm)	3.00	5.0	5.0
Pore volume (cm^3)	120.00	55.2	55.2
Porosity (%)	37.40	20.00	20.00
Permeability (Darcy)	0.235	0.603	0.603
Initial fluid	Aqueous solution of ClNa (1%)	Aqueous solution of ClNa (2%)	Aqueous solution of ClNa (2%)
Injected fluid	Aqueous solution of ClNa (1%) + $I^{131}Na$	Aqueous solution of ClNa (2%) + Tritium	Aqueous solution of ClNa (2%) + Comercial Polymer 454 (600ppm)

TABLE 1: Porous media and fluid characteristics

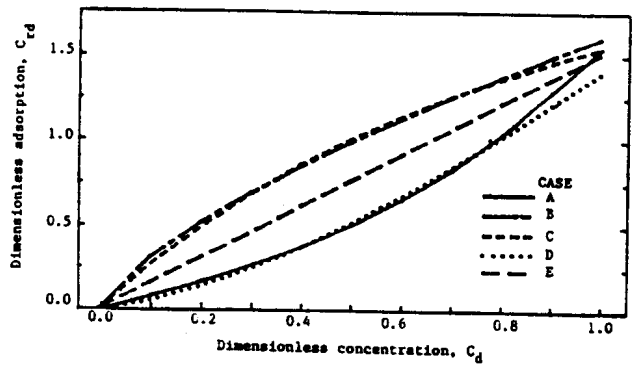

FIGURE 2: Langmuir's, Freundlich's and linear adsorption isotherms for cases B, C, D and E of Table 2. Levenberg-Marquardt's optimization method was used in the graphical representation (NSIG =3).

Adsorption model		A:Langmuir		B:Freundlich		C:Langmuir	D:Freundlich	E:Linear
Optimization method		Complex of Box	Levenberg-Marquardt	Complex of Box	Levenberg-Marquardt	Levenberg-Marquardt		
		varying three parameters		varying three parameters		fixing Pe, varying k_3, b	fixing Pe, varying k_2,n	varying Pe , k_1
PARAMETERS	Pe	29.6	29.7	5.68	5.53	5.53	29.7	8.67
	k_3, k_2 or k_1	0.737	0.736	1.61	1.61	2.63	1.41	1.52
	b or n	-0.539	-0.540	0.716	0.718	0.827	1.45	-----
FOx10^2		0.149	0.149	0.192	0.192	0.258	0.782	0.311
$\sqrt{FO/N}$ x10^2		0.936	0.936	1.96	1.96	1.23	2.63	1.35

TABLE 2: Aqueous solution of INa tagged with I^{131} flooding. A- Peclet Number (Pe) and Langmuir's adsorption parameters (k_3 and b). Comparison of results obtained by Complex of Box's and Levenberg-Marquardt's methods varying the three parameters simultaneously. B- Idem A, but the Freundlich adsorption model varying Pe, k_2 and n. C- Results obtained for the Langmuir model and Levenberg-Marquardt's method by fixing Pe and varying k_3 and b. D- Idem C, but Freundlich's model varying k_3 and b. E- Results obtained for the linear adsorption model varying simultaneously Pe and k_1. All the results were obtained with a convergence criterion of NSIG = 3 or COTA= 0.001.

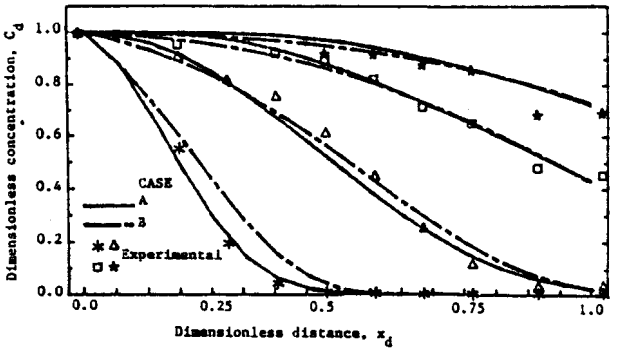

FIGURE 3 : Aqueous solution of INa tagged with I^{131} flooding. Dimensionless concentration as a function of dimensionless distance from inlet. Comparison among experimental data and results for different adsorption models (Freundlich's and Langmuir's). Levenberg-Marquardt's optimization method was used in the graphical representation (NSIG=3).

Cases	A	B	C	D	E
E_{exp}	0.101	0.110	0.121	0.147	0.113
$\sqrt{(E_{exp}/(N+M))}$	0.0498	0.0513	0.0536	0.0591	0.0519
E_A	------	0.0617	0.0788	0.0431	0.0356
$\sqrt{(E_A/(N+M))}$	------	0.0441	0.0433	0.0328	0.0291

TABLE 3: Aqueous solution of NaI tagged with I^{131} flooding. Global errors with respect to experimental data (E_{exp}) and with respect to case A (E_A). Cases A, B, C, D, and E have the same meaning as in Table 2.

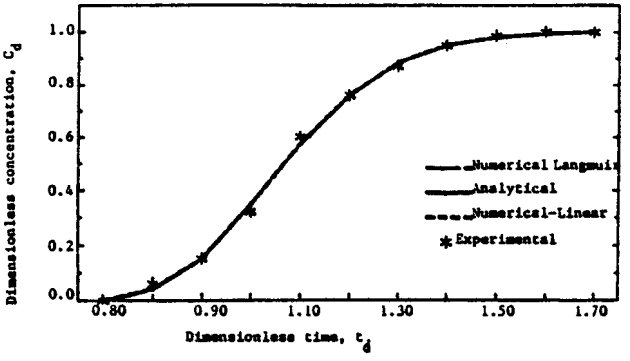

FIGURE 4: Aqueous solution of two-percent NaCl tagged with tritium flooding. Dimensionless concentration as a function of dimensionless time at outlet. Comparison between experimental data and results obtained by the Levenberg-Marquardt method using the numerical model and the analytical solution.

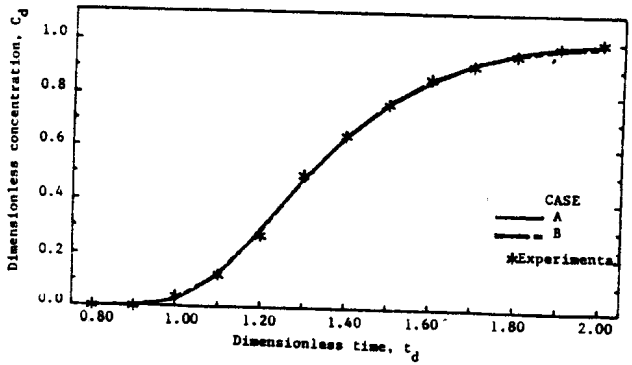

FIGURE 5 : Aqueous solution of two-percent NaCl with commercial Polymer 454 displacement. Dimensionless concentration as a function of dimensionless time at outlet. Comparison among experimental data and results estimated for different adsorption models (Freundlich's and Langmuir's). The Levenberg-Marquardt otpimization method was used in the graphical representation (NSIC=3).

Adsorption model		A:Langmuir		B:Freundlich		C:Linear	
Optimization method		Complex of Box	Levenberg-Marquardt	Complex of Box	Levenberg-Marquardt	Levenberg-Marquardt	
Mathematical model		Numerical		Numerical		Numerical	Analytical
PARAMETERS	Pe	72.6	71.4	72.7	73.6	72.2	72.9
	k_3, k_2 or k_1	0.0749	0.0788	0.0764	0.0763	0.0765	0.0829
	b or n	-0.0193	0.0388	1.01	1.04	-----	-----
FOx10^2		0.211	0.210	0.210	0.210	0.211	0.214
$\sqrt{(FO/N)}$ x10^2		1.45	1.45	1.45	1.45	1.45	1.46

TABLE 4: Aqueous solution of two-percent ClNa tagged with tritium flooding. A- Peclet number (Pe) and Langmuir's adsorption parameter k_3 and b). Comparison of results obtained by Complex of Box's and Levenberg-Marquardt's methods, varying the three parameters simultaneously. B- idem A, but Freundlich's adsorption model, varying Pe , k_2 and n. C- Peclet number and linear adsorption parameter (k_1). Comparison of results obtained by Levenberg-Marquardt's method in conjunction with the numerical model and the analytical solution. All the results were obtained with a convergence criteria of NSIC= 3 or COTA= 0.001.

Adsorption model		A:Langmuir	B:Freundlich	C:Langmuir	D:Freundlich	E:Linear
Optimization method		Levenberg-Marquardt				
		varying three parameters	varying three parameters	fixing Pe, varying k_3, b	fixing Pe, varying k_2, n	varying Pe, k_1
PARAMETERS	Pe	254	44.5	44.5	254	87.8
	k_3, k_2 or k_1	0.172	0.346	0.525	0.328	0.336
	b or n	-0.498	0.744	0.547	1.62	-----
FOx10^2		0.157	0.116	0.286	1.82	0.282
$\sqrt{(FO/N)}$ x10^2		0.944	0.902	1.31	2.91	1.53

TABLE 5: Aqueous solution of two-percent ClNa with commercial Polymer 454 displacement. A- Peclet number (Pe) and Langmuir adsorption parameter (k_3 and b). Results obtained by Levenberg-Marquardt's method NSIG = 3) varying the three parameters simultaneously. B- Idem A, but the Freundlich adsorption model varying Pe , k_2 and n . C- Results obtained for the Langmuir model by fixing Pe and varying k_3 and b. D- Idem C, but Freundlich model varying k_2 and n. E- Results obtained for the linear adsorption model varying simultaneously Pe and k_1.

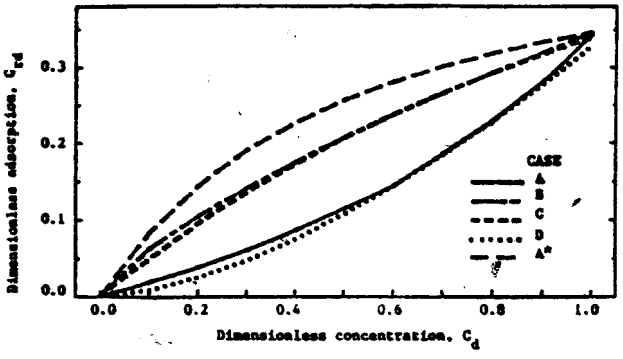

FIGURE 6: Langmuir's and Freundlich's adsorption isotherms for cases A, B, C, D and A* of aqueous solution of two-percent NaCl with commercial Polymer 454 displacement. Levenberg-Marquardt's optimization method was used in the graphical representation (NSIG=3).

COTA	FOx10^2	$\sqrt{(FO/N)}$x10^2	Pe	k_3	b
0.100000	0.131	1.04	188	0.186	-0.455
0.050000	0.131	1.04	188	0.186	-0.455
0.025000	0.131	1.04	188	0.186	-0.455
0.010000	0.131	1.04	188	0.186	-0.455
0.005000	0.187	0.944	254	0.172	-0.499
0.002500	0.187	0.944	254	0.172	-0.499
0.001000	0.187	0.944	254	0.172	-0.499
0.000005	0.187	0.944	254	0.172	-0.499

TABLE 6: Variation of the objective function, the mean residual error per measurement and the optimal parameters with the Complex of Box stopping criterion. Data from case A of Table 7

Initial values			Final values			Objective function values	
Pe	k_3	b	Pe	k_3	b	with experimental data points	with case A
10.0	0.172	-0.499	29.5	0.983	1.84	0.100x10^{-2}	0.784x10^{-6}
252	1.00	-0.495					
500	1.00	0.900					
500	0.172	-0.495	254	0.172	-0.499	0.187x10^{-2}	0.665x10^{-3}
252	0.172	-0.900					
187	0.200	-0.500					

TABLE 7: Aqueous solution of Polymer 454/brine displacement. Influence of initial values of the parameters on the final values obtained by applying Langmuir's adsorption model and Levenberg-Marquardt's optimization technique (NSIC = 3).