Coupling Effect of non-Linearity and Chemical Heterogeneity on Reactive Solute Transport in a Fixed Bed

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This study investigated the coupling effect of non-linearity adsorbed solute dispersion and chemical heterogeneity on reactive solute transport. This latter is applicated in a fixed bed at laboratory scale, in porous media. Following the approach of continuous media, and taking into account the discrete chemical heterogeneity distribution of the adsorbate, we have developed a model of adsorption in a fixed bed, by introducing a new parameter quantifying the chemical heterogeneity. Highlighting the influence of heterogeneity on the breakthrough curve required a resolution of the advection-dispersion equation, which obtained from the modeling. In our case, we have used an effective numerical method which is the Finite Volume Method, to discretize the partial differential equation obtained. Our work is based on experimental data from the study of (Salman, et al, 2011). Numerical results show that the nonlinear interactive solute transport in a chemical heterogeneous medium differs from that in the homogeneous one. This result is deduced from the difference between the breakthrough curves of the two cases. The breakthrough curve is more spread when chemical heterogeneity of the medium is more important. Fixing the heterogeneity of the medium, we have found that the porous media length has also an effect.

1. Introduction

The study of porous media is a very active field of research because of its wide applications. In this media, the transport of reactive solute is the result of many processes which are the three main convection, dispersion and adsorption. Based on conventional models describing the adsorption in fixed bed, the chemical homogenous medium is known as a uniform distribution of active sites on the entire solid. In most cases, the different model represents pretty well the actual behavior of adsorbates. However, with the development of new supports fixed beds consisting of solids of various kinds, particularly in operations in small columns (columns of laboratory, chromatographic, domestic uses filters, etc...), there is a spatial integral of active sites in the medium. This distribution is called chemical heterogeneity of the adsorbate. Ignoring the effect of the chemical heterogeneity in modeling, the breakthrough curve induces errors that affect the efficiency of the column and the size of the bed. The development of simulation tools in column adsorption processes becomes increasingly necessary with the great interest in fixed bed processes and transport in porous media. Process simulation of fixed bed adsorption depends on the model of transport and interactions. Taking into consideration the exchange phenomena leading and recess of the law adequately insulated. The solution of the resulting equation shows a breakthrough curve which constitutes the basic element of design of a bed on an industrial scale. Solving the equation usually requires a numerical solution, depending on the complexity of the model. There are very few researches (Semra, et al, 2008), (Metzger, et al, 1996), studied the non-linear adsorption effect on the solute transport in chemical heterogeneous porous media. Primarily, we are interested in this work to solve the transport equation of solute adsorbed on the solid chemical heterogeneous porous media. Secondary, we present the effect of coupling non-linearity and chemical heterogeneity on the transport of reactive solute in a fixed bed. Finally, we show the effect of the length of the column on the breakthrough curve.

2. Solute transport in chemical heterogeneous medium

The medium is assumed to be composed of two types of layers, active and non-active ones uniformly alternated. Active and non-active layers thicknesses are respectively l_1 and l_2 shown in Figure1.
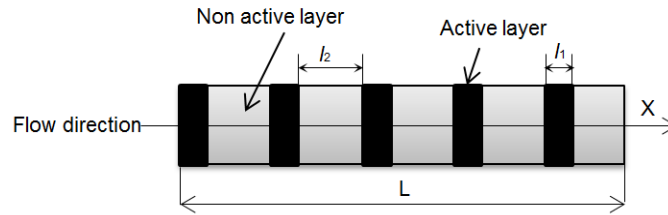

Figure 1: One-dimensional fixed bed chemical heterogeneity scheme.

Chemical heterogeneity distribution is accounted by the probability distribution $\Gamma(x)$ for a solute molecule to meet an active grain in the flow direction x:

$$\Gamma(x) = \begin{cases} 1, \text{for active layer} \\ 0, \text{for non active layer} \end{cases}$$

<div align="right">(1)</div>

The mean value of the distribution is γ defined by $\gamma = \dfrac{l_1}{l_1 + l_2}$

In heterogeneous media, linear adsorption into fixed beds is described by the one-dimensional advection-dispersion equation (Sardin, 1993) and (Zheng, et al. 1995) is written such:

$$u\frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} + \frac{1-\varepsilon}{\varepsilon}\frac{\partial C_p}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2}$$

<div align="right">(2)</div>

Where u is the linear flow velocity; C, the fluid in flow concentration; C_p the aggregate concentration; D_L, the hydrodynamic dispersion coefficient; ε, the extra aggregate porosity; x, the flow direction.
Considering a non-linearly adsorbed solute using Freundlich isotherm under equilibrium conditions, the solid phase concentration is

$$C_p(x,t) = \rho_p \, \Gamma(x) K_f \, C^n$$

<div align="right">(3)</div>

Substituting these terms in the resulting equation (Equation 1), we obtain the final equation.

$$\mathrm{U}.\frac{\partial \mathrm{C}}{\partial x} + \frac{\partial \mathrm{C}}{\partial t}\left[1 + \rho\left(\frac{1-\varepsilon}{\varepsilon}\right)\Gamma(x)\mathrm{K_F}.n.\mathrm{C}^{\,n-1}\right] = \mathrm{D_L}\frac{\partial^2 \mathrm{C}}{\partial x^2}$$

<div align="right">(4)</div>

Where ρ is the bulk density, n and K_F are the Freundlich constant and distribution coefficient, respectively.
Using the following dimensionless variable

$$T = t/t_0 \; ; t_0 = \varepsilon V/Q \; ; X = x/d_p \; ; C^* = C/C_0 \; .$$

<div align="right">(5)</div>

Where t_0 and d_p are respectively the mean fluid passage time (or the advection characteristic time) and the particle means size, the adsorbed dimensionless equation becomes:

$$\frac{\partial C^*}{\partial X} + \frac{d_p}{L}\left(1 + \Gamma(X)\rho_p \, C_0^{*\,n-1} \, n K_f \, C^{*\,n-1}\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial C^*}{\partial T} = \frac{D_L}{U}\frac{\partial^2 C^*}{\partial X^2}$$

<div align="right">(6)</div>

The initial condition is $C^*(X,0) = 0$ and, in view the applications, the boundary conditions are a Dirichlet condition (given concentration) $C^*(0,t^*) = 1$ at the inlet and zero diffusive flux $\left(\dfrac{\partial C}{\partial X}\right)_{L/d_p} = 0$ at the outlet.

The dimensionless equation has solved using the finite volumes method according to the Second Order Backward and using the Adam Bashforth scheme (Wesselin, 2001).

The effect of chemical heterogeneity that is investigated, considered the breakthrough curve ($C^*(L,t)$) spreading versus the chemical heterogeneity scale. The latter is chosen equal to the inverse of the mean value of the probability distribution, $1/\gamma$. This assumption is analogous to the one adopted by (Semra, et al 2009). In fact, the thicker than the non-active the active layer is, the less heterogeneous the medium is. According to the residence time distribution theory (Pivovarov, 2005), the breakthrough curves spreading is accounted for by the second order central moment σ^2 and the reduced variance σ'^2, given by:

$$\sigma^2 = \int_0^\infty 2t\left(1 - C^*(t)\right)dt - \mu_1^2 \tag{7}$$

The reduced variance, σ'^2 accounts for solute effective dispersion and is calculated by:

$$\sigma'^2 = \frac{\sigma^2}{\mu_1^2} \tag{8}$$

Where μ_1 is the mean retention time (Villermaux, 1993).

$$\mu_1 = \int_0^\infty \left(1 - C^*(t)\right)dt \tag{9}$$

So, breakthrough curves are exploited plotting C/C0 versus t/μ_1 then with another exploitation σ'^2/σ'^2_w versus $1/\gamma$ where σ'^2_w corresponds to a water tracer breakthrough curve spreading. It is only function of hydrodynamic dispersion and equal to one obtained for a linearly adsorbed solute into homogeneous medium. The ratio σ'^2/σ'^2_w excludes then the effect of hydrodynamics on the relation between chemical heterogeneity distribution and the contact time (as it is directly related to the spreading). Hence, it accounts for the net increase of dispersion due to chemical heterogeneity.

First, we took the experimental data of the study of (Salman, et al 2011), which are grouped in tables (1,2,3) by making an adjustment with the results obtained numerically. After that, a comparison between the case of chemically homogeneous and chemically heterogeneous is made to prove the effect of the chemical heterogeneity. In the following, chemical heterogeneity is taken into account in the fixed bed non-linear adsorption equation in order to investigate its effect on solute effective dispersion at different levels of heterogeneity. Finally, the relationship between chemical heterogeneity and dispersion is observed as a function of medium length.

Table 1: Properties of the adsorbent

Adsorbent	Density ρ (g/dm^3)	Porosity ε	Particle diameter d_p (m)
PalmFrond activated carbon	2260	0.45	0.00125

Table 2: Properties of the adsorbate

Adsorbate	Concentration C_0 (mg/l)	Debit Q (m^3/s)	Freundlich constant K_f (g^{1-n}.m^{3n}.g^{-1})	Freundlich constant n
2,4-D dichlorophenoxyacetic	100	0.167E-06	8.74	0.713

Table 3: Column Properties

Column length L(m)	Column diameter D(m)
0.03	0.012

3. Results and Discussions

In order to validate our numerical results, we used the experimental data of the study of (Salman et al, 2011). The results are shown in Figure 2. The representation has given two curves of the same shape. This means that our simulation results are in good agreement with experimental values obtained by (Salman et al, 2011).
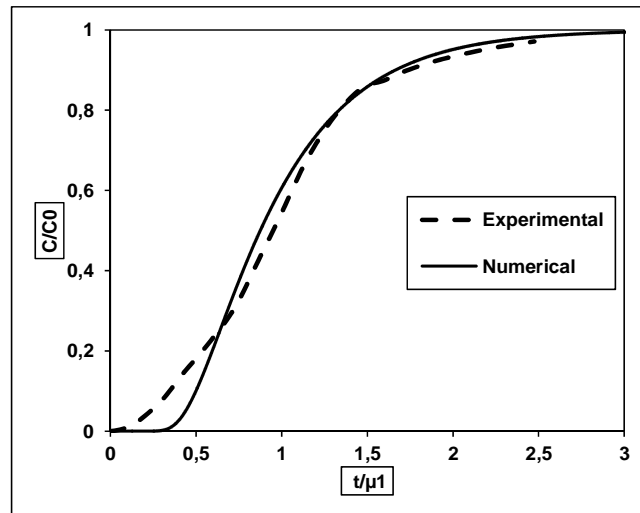

Figure 2: Adjustment between numerical and experimental breakthrough curves represented on time reduced on the moment of order one.

3.1 Existence of the effect of chemical heterogeneity

To prove the existence of the influence of chemical heterogeneity, we set it to a value γ =0.166 (Gam in the figures represents the proportion of active grains γ). The result shows that the two breakthrough curves have the same gait but with a large gap (Figure 3). This difference confirms that the adsorption of solute non-linearly interactive in a chemical heterogeneous medium, differs from that in the case of chemically homogeneous.
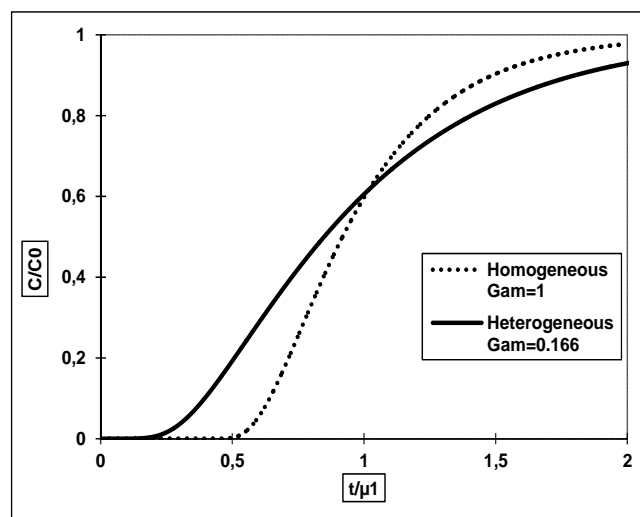

Figure3: Comparison between chemically homogeneous and heterogeneous media.

3.2 Effect of Variation of chemical heterogeneity

In order to understand the effect of chemical heterogeneity on the dispersion, we were varied the proportion of active grains (γ) from 0 to 1. Breakthrough curves obtained are shown in Figure 4. The graphical representation of these curves showed that they have the same shape, with differences

varying the chemical heterogeneity of the medium. For a value gam = 1, it is the chemically homogeneous case, the curve is less spread out. By reducing this proportion, spreading becomes more important to the value gam = 0.166 (high chemical heterogeneity), it is the most spread out. We can explain the difference between these spreading by an additional concentration gradient which, depends on the variation of the chemical heterogeneity of the medium. Indeed, presence of intensely active zones on the adsorbent next to nonactive ones creates important solute concentration gradients. The fluid close to the active zones is very poor of solute because of solid retention, whereas the fluid close to nonactive zones is very rich in solute.
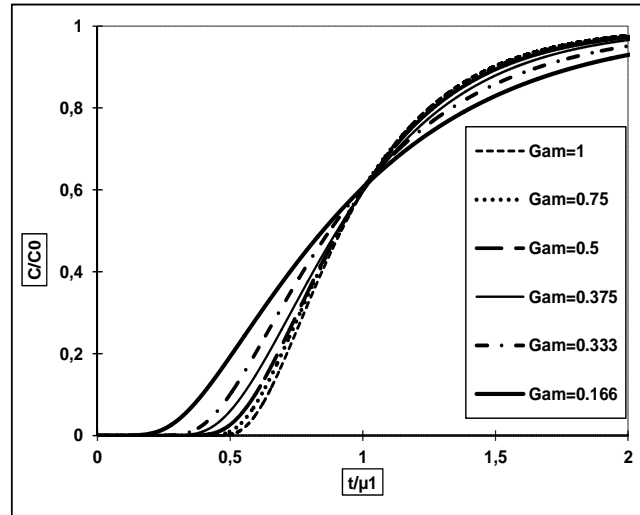

Figure 4: Effect of chemical heterogeneity on breakthrough curves spreading.

3.3 Effect of the column length

For studying the effect of the column length, we were set to the chemical heterogeneity value γ =0.1 and by varying the column length, from 3 to 80cm. The results shown in Figure 5 showed a non-monotonic variation of the effect of the length. For a length of 80cm, the curve is less spread out. By reducing this length, the breakthrough curve becomes more spread out (for L = 40cm). By cons, if further decreases to a value of length of 19.5 cm, the breakthrough curve becomes less spread, which is not the case if we reduce the length another time, the breakthrough curve becomes the most spread out.
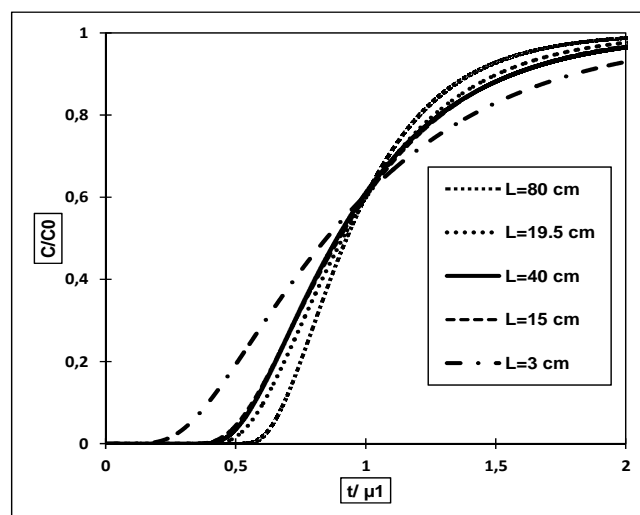

Figure 5: Effect of the column length on the spreading of the breakthrough curves.

Calculation of breakthrough curves variances led to a linear variation of the ratio σ'^2/σ'^2_w with heterogeneity. The slope, which is normally null and independent from interaction and column length according to the linear adsorption in fixed beds theory, is found for heterogeneous media function of medium scale as shown in Figure 6. All the variations start from the value 1 which corresponds to the unique value expected by the theory when chemical heterogeneity is not taken into account.
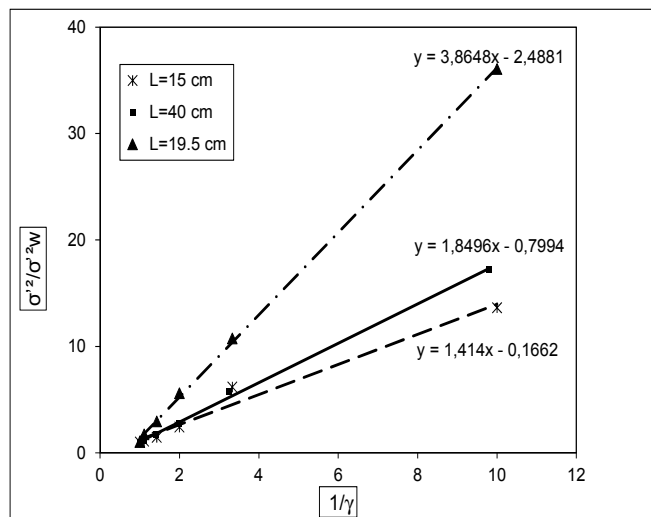

Figure 6: Effect of chemical heterogeneity distribution on breakthrough spreading at different column length.

4. Conclusion

This article aimed at showing and modeling the effect of the coupling of a new parameter wish is the chemical heterogeneity with non-linearly adsorbed solute, in porous media on global dispersion of the breakthroughs. Results show a non-superposition of the breakthrough curves between homogeneous medium and heterogeneous one, the dispersion of this latter increase with chemical heterogeneity of the medium. The noticed increase of breakthrough curves at small scale shows that one can no longer ignore chemical heterogeneity in predicting the breakpoint, and thus the contact time necessary for a fixed bed adsorption operation. However, medium length seems to create nonmonotonous variation of dispersion because of the heterogeneity.

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