

Effect of Medium Capacity on the Relationship between Chemical Heterogeneity and Linearly Adsorbed Solute Dispersion into Fixed Beds

K. Kaabeche-Djerafi, N. Bendjaballah-Lalaoui, and S. Semra

Abstract—The paper aims at investigating influence of medium capacity on linear adsorbed solute dispersion into chemically heterogeneous fixed beds. A discrete chemical heterogeneity distribution is considered in the one-dimensional advective-dispersive equation. The partial differential equation is solved using finite volumes method based on the Adam-Bashforth algorithm. Increased dispersion is estimated by comparing breakthrough curves second order moments and keeping identical hydrodynamic properties. As a result, dispersion increase due to chemical heterogeneity depends on the column size and surprisingly on the solid capacity. The more intense capacity is, the more important solute dispersion is. Medium length which is known to favour this effect vanishing according to the linear adsorption in fixed bed seems to create nonmonotonous variation of dispersion because of the heterogeneity. This nonmonotonous behaviour is also favoured by high capacities.

Keywords—linear adsorption; chemical heterogeneity; dispersion; fixed bed; porous media

I. INTRODUCTION

IN presence of nonhomogeneous chemical activity distribution of adsorbents into fixed beds, effective dispersion of linearly adsorbed solute is found no longer equal to the one of a water tracer. Assessing both tracers effective dispersion by the reduced variance of their respective breakthrough curves, Semra *et al.* [1]-[2] emphasized an increasing reduced variance with the chemical heterogeneity chosen parameter for identical hydrodynamics. This finding suggests that transport and interaction are no longer independent from each other. Hence, this article aims at showing interaction influence on interacting solutes transport into chemically heterogeneous porous media at different column lengths.

In homogenous media, linear adsorption into fixed beds is described by the one-dimensional advection-dispersion equation [3]-[4]:

$$u \frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \frac{\partial q}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} \quad (1)$$

K. Kaabeche-Djerafi is with the Department of Industrial Chemistry, University Mentouri of Constantine (UMC), BP 325, Route Ain El Bey, 25017 Constantine, Algeria (email: kaabeche_khatima@yahoo.fr)

N. Bendjaballah-Lalaloui is with the Department of Industrial Chemistry, University Houari Boumédiène of Sciences and Technology (USTHB), BP 32 El Alia, 16111 Bab Ezzouar, Algiers, Algeria (email: nadia_bendjaballah@yahoo.fr)

S. Semra (corresponding author) is with the Department of Industrial Chemistry, University Mentouri of Constantine (UMC), BP 325, Route Ain El Bey, 25017 Constantine, Algeria (email: safia.semra@yahoo.fr)

Where u is the linear flow velocity; C , the fluid in flow concentration; q , the aggregate concentration; D_L , the hydrodynamic dispersion coefficient; ε , the extra aggregate porosity; x , the flow direction.

q and C are related through α , the distribution coefficient between the solid and the mobile fluid phases. α takes into account transfer phenomena between mobile and aggregate immobile fluid phases, and adsorption thermodynamics [5].

$$q = \alpha C \quad (2)$$

When phase and thermodynamic equilibria are assumed, linear adsorption distribution coefficient is constant and reduces to the thermodynamic equilibrium constant K_d . Equation (1) becomes:

$$u \frac{\partial C}{\partial x} + [1 + K'_d] \frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} \quad (3)$$

Where K'_d is called the global medium capacity and is related to the thermodynamic distribution coefficient K_d through:

$$K'_d = \rho_p \frac{1-\varepsilon}{\varepsilon} K_d \quad (4)$$

ρ_p is the bulk density.

Solution to the adsorption equation can be derived using the Laplace transform technique. The breakthrough curve data are obtained by inversion of the Laplace transform. However, one can derive the breakthrough curve moments without solving equation (3) by using the transfer function $G(s)$ relating $\bar{C}(L)$ and \bar{C}_0 , the Laplace transforms of inlet and outlet fluid concentrations respectively. Breakthrough k^{th} order moment is derived according to the Van Der Laan relation [6]:

$$\mu_k = (-1)^k \left. \frac{\partial^k G(s)}{\partial s^k} \right|_{s=0} \quad (5)$$

The most important moments are the first order one, μ_1 , which assesses the mean residence time, and the second one, μ_2 , which leads to the breakthrough curve variance, σ^2 , according to the following expression:

$$\sigma^2 = \mu_2 - \mu_1^2 \quad (6)$$

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

$$\sigma'^2 = \frac{\sigma^2}{\mu_1^2} \quad (7)$$

One can define an effective flow velocity for sorbing solute displacement, u_r , and an effective dispersion coefficient D_{Lr} such as:

$$u_r = \frac{u}{1 + \frac{1-\varepsilon}{\varepsilon} \rho K_d} \quad (8)$$

$$D_{Lr} = \frac{D_L}{1 + \frac{1-\varepsilon}{\varepsilon} \rho K_d} \quad (9)$$

Adsorption equation becomes:

$$u_r \frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} = D_{Lr} \frac{\partial^2 C}{\partial x^2} \quad (10)$$

This equation is identical to a water tracer transport assuming phase equilibrium. A column Peclet number for the adsorbed solute can be derived such as:

$$Pe_r = \frac{u_r L}{D_{Lr}} \quad (11)$$

Thus:

$$Pe_r = \frac{uL}{D_L} = \quad (12)$$

On the other hand, breakthrough curve moments are the following [3]-[6]:

$$\mu_1 = t_0(1 + K'_d) \quad (13)$$

Where t_0 is the mean residence time for water tracer.

$$\sigma_r^2 = \frac{2}{Pe_r} = \frac{2}{Pe} = \sigma_w^2 \quad (14)$$

Where σ_r^2 and σ_w^2 are respective reduced variances for adsorbed solute and water tracer.

On can find finally:

$$\sigma_r^2 = \frac{2D_L}{uL} \quad (15)$$

The reduced variance contains no parameter referring to the interaction. It implies that for the same media hydrodynamic characteristics, the ratio σ_r^2 / σ_w^2 is equal to 1 whatever the medium capacity is. This equality can be considered as a reference value comparing to which any influence of any other parameter can be assessed. In the following, chemical heterogeneity is taken into account in the fixed bed linear adsorption equation in order to investigate its effect on solute effective dispersion at different levels of heterogeneity. Mainly, capacity medium influence on the relationship between chemical heterogeneity and dispersion is observed as a function of medium length.

II. METHODS

Considering chemical heterogeneity as nonuniform distribution of active sites into the medium (in other words chemical activity distribution of the medium), the considered granular medium is composed of two types of layers, active and nonactive ones uniformly alternated. Active and nonactive layers thicknesses are respectively l_1 and l_2 .

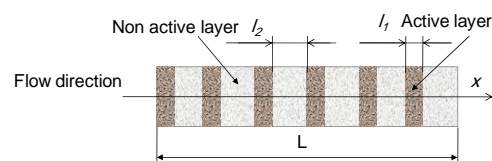


Fig. 1 One-dimensional fixed bed chemical heterogeneity scheme

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

$$\Gamma(x) = \begin{cases} 1, & \text{for active layer} \\ 0, & \text{for non active layer} \end{cases} \quad (16)$$

The mean value of the distribution is γ defined by:

$$\gamma = \frac{l_1}{l_1 + l_2} \quad (17)$$

Both active and nonactive layers thicknesses are proportional to a particle mean diameter d_p .

Heterogeneous fixed bed adsorption is accounted for by (1) taking into account:

$$q(x, t) = \rho_p K_d C(x, t) \Gamma(x) \quad (18)$$

Using dimensionless variables, the adsorbed equation becomes:

$$\frac{\partial C^*}{\partial X} + \alpha \left(1 + \Gamma(X) \rho_p K_d \frac{1-\varepsilon}{\varepsilon} \right) \frac{\partial C^*}{\partial T} = \beta \frac{\partial^2 C^*}{\partial X^2} \quad (19)$$

Where:

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

$$\beta = D_L/d_p u$$

The dimensionless equation is solved using the finite volumes method according the Second Order Backward and using the Adam Bashforth scheme [7]. The following initial and limit conditions are considered:

$$C^*(X, 0) = 0, \quad C^*(0, t^*) = 1, \quad \left(\frac{\partial C^*}{\partial X} \right)_{L/d_p} = 0$$

The effect of chemical heterogeneity is investigated considering 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. [1]. In fact, the thicker the active layer is, the less heterogeneous the medium is.

According to the residence time distribution theory, the breakthrough curves moments are calculated by [6]:

$$\mu_1 = \int_0^\infty (1 - C^*(t)) dt \quad (20)$$

$$\sigma^2 = \int_0^\infty 2t (1 - C^*(t)) dt - \mu_1^2 \quad (21)$$

The medium global (mean) capacity, said also the dimensionless distribution coefficient, is function of the mean probability of activity distribution via:

$$K'_d = \gamma \frac{1-\varepsilon}{\varepsilon} \rho_p K_d \quad (22)$$

So, breakthrough curves are exploited plotting σ'^2/σ'^2_w versus $1/\gamma$. The ratio σ'^2/σ'^2_w excludes then the effect of hydrodynamics on the relation between chemical heterogeneity. Hence, it accounts for the net increase of dispersion due to chemical heterogeneity. Effect of chemical heterogeneity is evaluated at different bed lengths for the same heterogeneity distribution and also at different global capacities. Model constant parameters are the following: the flow rate $Q = 1 \text{ cm}^3/\text{s}$; $d_p = 4 \times 10^{-4} \text{ cm}$; $\rho_p = 2,6 \text{ g/cm}^3$; $\varepsilon = 0,48$, $l_l = 50 d_p$. The hydrodynamic dispersion coefficient is calculated according to [8]:

$$D_L = 4 d_p u \quad (23)$$

III. RESULTS AND DISCUSSION

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 and capacity as shown in figures 2-5. 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.

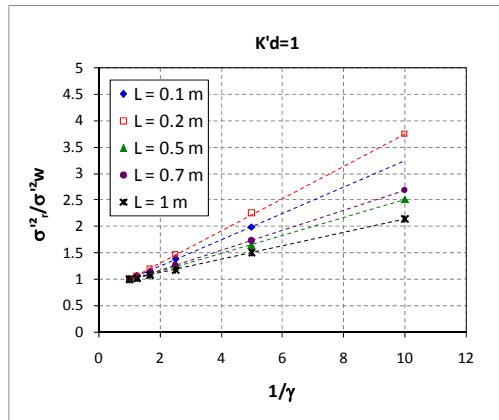


Fig. 2 Dispersion increase due to chemical heterogeneity at different medium lengths L , global capacity $K'_d=1$

The plot of the slope with column length at different medium capacities showed a polynomial variation (figure 6). In chemically homogeneous medium, this slope decreases linearly versus the medium length (equation (15)). The line is unique for all medium capacities.

Figure 6 shows an intensified effect of heterogeneity through high capacities. However, medium length which is known to favour this effect vanishing (equation (15)) seems to create nonmonotonous variation of dispersion because of the

heterogeneity. This nonmonotonous behaviour is also favoured by high capacities.

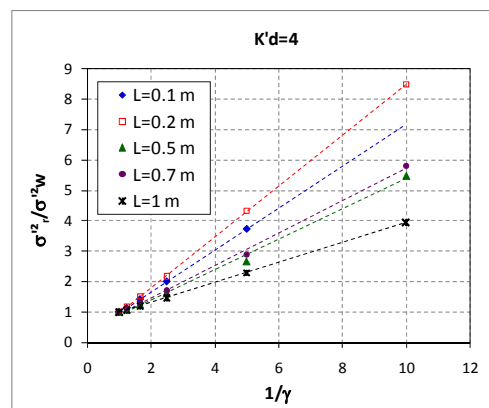


Fig. 3 Dispersion increase due to chemical heterogeneity at different medium lengths L , global capacity $K'_d=4$

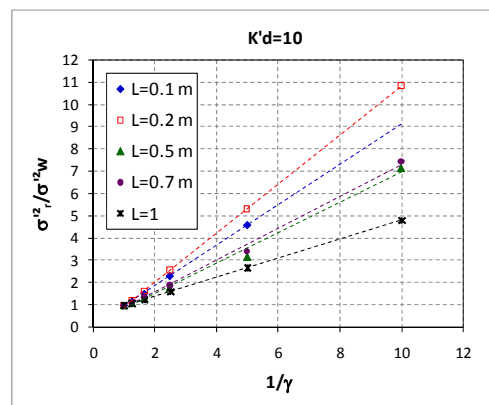


Fig. 4 Dispersion increase due to chemical heterogeneity at different medium lengths L , global capacity $K'_d=10$

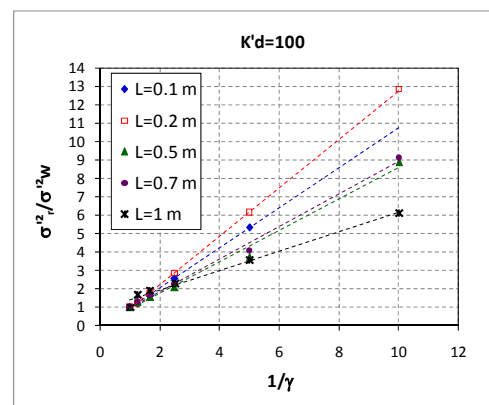


Fig. 5 Dispersion increase due to chemical heterogeneity at different medium lengths L , global capacity $K'_d=100$

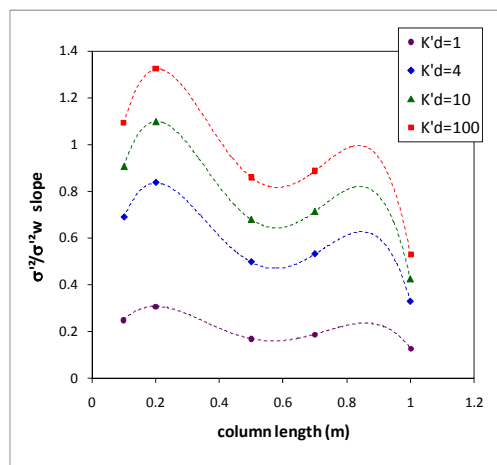


Fig. 6 Variation of the slope of linear dispersion increasing due to chemical heterogeneity at different medium lengths L and different global capacities

The fact that intense medium capacity amplifies chemical heterogeneity effect can be physically explained considering the same heterogeneity level, i.e., the same distribution of solid activity into 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. The more intense the capacity is, the more important solute concentration gradients are and, thus, the more important solute dispersion is.

However, nonregular effect of medium scale on the relation between heterogeneity and dispersion is not clear yet. Actually, one expected a monotonous decrease of the slope as the medium scale increases. In fact, medium length represents the physical heterogeneity scale and as it becomes greater than the chemical heterogeneity one, the effect of chemical heterogeneity on solute dispersion would decrease regularly [9].

REFERENCES

- [1] S. Semra, M. Sardin, and M. O. Simonnot, "Effect of Chemical Heterogeneity on Adsorbed Solute Dispersion at Column Scale", *AIChE J.*, vol. 54, no 4, pp 950-956, 2008.
- [2] S. Semra, M. Sardin, and M. O. Simonnot. "A New Mixing-Cell-in-Series Model to Predict Breakthrough Curve in Chemically Heterogeneous Media at Column Scale", *Chemical Product and Process Modeling*, vol. 4 Iss. 1, Art. 31, 2009.
- [3] M. Sardin, "Modélisation du transport transitoire de solutés en milieux poreux : Les modèles linéaires", 1993, *Sciences Géologiques, Bulletin* N° 46, pp 197-216.
- [4] C. Zheng and G. D. Bennett. "Applied contaminant transport modeling : Theory and practice". USA : Van Nostrand Reinhold, 1995, 440 p.
- [5] M. SRADIN et al. "Modeling the nonequilibrium transport of linearly interacting solutes in porous media : A Review". *Water Resources Research*, vol. 27, no 9, pp 2287-2307, 1991.
- [6] J. Villiermaux. "Génie de la réaction chimique : Conception et fonctionnement des réacteurs". Paris, France : TEC & DOC-LAVOISIER, 1993, 448 p.
- [7] A. Bisio, R. L. Kabel, "Scaleup of chemical processes : Conversion from laboratory scale tests to successful commercial size design", John Wiley & Sons, Inc., New York, U.S.A, 1985.
- [8] S. Pivovarov, "Dispersion of compounds in transport processes: Velocity dispersion model", *J. of Colloid and Interface Science*, vol. 289, pp 600-603, 2005.
- [9] M. Sahimi. "Flow and transport in porous media and fractured rock: From classical methods to modern approaches". Germany : VCH Verlagsgesellschaft mbH, 1995, 482 p.