Effect of Chemical Heterogeneity on Adsorbed Solute Dispersion at Column Scale

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Chemical heterogeneity seems to be responsible for spreading increase of adsorbed solute breakthrough curves. Adsorption in fixed beds assumes chemically homogeneous media. However, this is not always true, in particular when natural sands or mixed adsorbent filters are used in drinking water purification. Neglecting eventual effect of chemical heterogeneity may engender false modeling bases. So, considering homogeneous grain size distribution, the effect of chemical heterogeneity on global dispersion in porous media has been investigated experimentally in this article at column scale. Breakthroughs of adsorbed solute showed a visible effect of chemical heterogeneity on solute global dispersion increasing. The more heterogeneous the medium, the more spread the adsorbed solute breakthrough. Reduced variance showed a linear variation with the chemical heterogeneity scale at closely constant media global capacity. A pseudo-homogeneous model has been developed to simulate experimental data by increasing dispersion parameter. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 950–956, 2008

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Introduction

Adsorption has evolved as a major industrial separation process especially in trace contaminant elimination from drinking water, in treatment of industrial effluent containing toxic solutes, in gas purification, and as a drying process. Fixed beds of natural or synthetic media are usually used for performing adsorption processes. Modeling of adsorption in fixed bed allows to predict breakthrough curves when preliminary experiments cannot be carried on. Breakthrough curve is particularly interesting in adsorption processes as its spreading indicates operation efficiency and is directly related to solute plume global dispersion into the medium.[1]

Theoretically, plume dispersion is because of three phenomena occurring simultaneously.[2] First, the hydrodynamic dispersion, which is because of fluid surrounding grains, and is proportional to flow velocity and hydrodynamic dispersivity.[1] The latter is a medium geometric property that determines a sample dimension, the size where measured values of medium hydrodynamic properties are closely identical. Hydrodynamic dispersivity is also considered as the length of elementary representative volume (ERV) for hydrodynamics[3] and is about a few times the mean grain diameter. Also, it can be termed the scale of hydrodynamic dispersion heterogeneity. Other contributions to the global solute dispersion are either because of phase exchange, and eventually chemical kinetics, or because of isotherm nature.[2,4]

Consequently, breakthrough curve should be well estimated knowing hydrodynamic, kinetic, and thermodynamic parameters. However, transport of adsorbed solutes in some natural media at laboratory scale showed more spread breakthroughs than predicted with known models.[5–7] So, in order to fit experimental results, Appert-collin et al.[5] introduced some kinetic effects in modeling. This gave a best approximation of experimental curves than with equilibrium model but kinetic effects did not fit observed earlier break-

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through point. Lefèvre et al.[6] had had to increase empirically the hydrodynamic dispersion coefficient in order to fit experimental data. Increasing hydrodynamic dispersion coefficient seemed to give a good fitting as indicated by Villermaux and Antoine.[8] However, one may ask the why experimental curves were more spread than expected, and what does dispersion coefficient increase mean. Note that problems of spreading have been observed on some natural media.[5–7] So, increased global solute dispersion when no kinetic limitation is observed may come from activity distribution of porous media experimented. Indeed, if chromatography theory assumes a physically and chemically homogeneous medium, a soil sample activity could be variable not only on one grain but also at the aggregate or column scale, even if it looks homogeneous (uniform color and texture). Consequently, solute adsorbability would be variable and fluid phase concentration gradients would be created during solute transport, creating in turn supplementary dispersion phenomena. Hence, chemical heterogeneity seems to cause an increase in breakthrough curve spreading for adsorbed solute—what this article aims at checking experimentally.

Most of the papers dealing with solute transport in natural porous media consider heterogeneity at aquifer scale. Investigations generally neglect effect of chemical heterogeneity at aggregate scale because of predominance of permeability heterogeneity.[9–13] Nevertheless, Bellin and Rinaldo[11] noted the effect of distribution coefficient heterogeneity at aquifer scale only on longitudinal dispersion of linearly adsorbed solute, this effect depends however, on correlation degree of chemical and physical heterogeneities. Actually, effect of chemical heterogeneity if exists at aquifer scale vanishes at long distances from the inlet because of hydraulic conductivity heterogeneity.[14,15] Indeed, when the medium shows many types of heterogeneities, the transport parameters depend on the property in which the heterogeneity scale is the most important, and which is termed dominant heterogeneity[16]. However, medium permeability is homogeneous at laboratory or industrial scale, so chemical heterogeneity may have an important effect in particular when it is as important as hydrodynamic dispersivity. Sugita and Gillham[17–19] investigated the effect of chemical heterogeneity on adsorbed solute at column scale. They concluded that chemical heterogeneity accounted for by retardation factor distribution because of grain size distribution heterogeneity explains a major part of experimental breakthrough curve spreading. However, spreading was not completely accounted for by the model. So, this article focuses on chemical heterogeneity at column scale considering a homogeneous grain size distribution. As transport and retention effects on dispersion are independent from each other for linear equilibrium adsorption, this type of interaction is an ideal situation to distinguish the effect of chemical heterogeneity from any other influence. Investigation methodology consists of performing water and adsorbed solute tracing experiments on chemically heterogeneous media at column scale, calculating breakthrough curve moments and comparing water and adsorbed solutes behaviors. Simulation of breakthrough curves is accomplished according to "mixing cells in series" model. Experiments assume no kinetic limitation.

Materials and Methods

Dispersion parameter

A column Peclet number is calculated either for water tracer or adsorbed solute by:

$$\mathrm{Pe} = \frac{uL}{D_\mathrm{L}} \tag{1}$$

where L is the medium length.

According to linear chromatography theory, reduced variance that accounts for effective dispersion of solute plume is inversely proportional to the Peclet number and is the same either for water tracer or linearly adsorbing solute. It is related to hydrodynamic dispersion coefficient by:

$$\sigma_\mathrm{r}'^2 = \sigma'^2 \approx \frac{2D_\mathrm{L}}{uL} \tag{2}$$

where $\sigma_\mathrm{r}'^2$and σ'^2 are, respectively, reactive and inert solute reduced variance.

Remembering expression of hydrodynamic dispersion coefficient[3]:

$$D_\mathrm{L} = \alpha_\mathrm{L} u \tag{3}$$

one can derive the relation between reduced variance and hydrodynamic dispersivity:

$$\sigma_\mathrm{r}'^2 = \sigma'^2 = \frac{2\alpha_\mathrm{L}}{L} \tag{4}$$

α_L is the hydrodynamic dispersivity.

This result shows uncoupled linear equilibrium adsorption and hydrodynamic dispersion. Thus, comparison of breakthrough reduced variance either for adsorbed solute or water tracer shows whether chemical heterogeneity affects the solute transport at column scale or not.

Mixing cells in series model for homogeneous media

Simulation of breakthrough curves is accomplished using mixing cells in series model. In this section, basis of modeling into homogeneous media is remembered, and will be extended in a following section to the heterogeneous case. The mixing cells in series model is a global discrete approach that provides only global transport information, but enough to predict breakthrough curves in fixed beds.[20] The method consists of dividing the medium L long into J successive elements of equal size, called mixing cells or theoretical stages. The cell size is equal to the ERV:

$$\mathrm{ERV} = \frac{V}{J} \tag{5}$$

where V is bed volume.

As flow is one-dimensional, the cell size can be represented by L/J, which is called mixing length and is equivalent to hydrodynamic dispersivity. Mass balance in a k rank cell is:

$$QC_{k-1} = QC_k + \frac{\varepsilon V}{J}\frac{dC_k}{dt} + \frac{(1-\varepsilon)V}{J}\frac{dC_{p,k}}{dt} \tag{6}$$

Table 1. Characteristics of Chemically Heterogeneous Media

Column	Medium Length (cm)	Total Medium Mass (g)	Mass Ratio of Quartz (%)	Mass Ratio of Chromosorb (%)	Mass Ratio of HMN (%)	γ
1	6.6	6.97	95.6	4	0.4	0.59
2	7.3	8.13	97.6	2	0.4	0.39
3	7.3	8.45	98.6	1	0.4	0.24
4	5.1	5.92	99.1	0.5	0.4	0.18

where Q is flow rate, $[L^3 \cdot T]$; $C_{k,}$ fluid concentration in cell k, $[M \cdot L^{-3}]$; C_{k-1}, fluid concentration at the inlet of cell k, $[M \cdot L^{-3}]$; $C_{p,k}$, stationary concentration in cell k, $[M \cdot L^{-3}]$; ε, bed volume fraction occupied by mobile fluid phase.

Assuming linear equilibrium adsorption and using Laplace transform, transfer function between inlet and outlet mobile phase concentrations for one cell, $g_k(s)$, is given by:

$$g_k(s) = \frac{\bar{C}_k}{\bar{C}_{k-1}} = \left[1 + \frac{t_m s\left(1 + K'_d\right)}{J}\right]^{-1} \tag{7}$$

where s is the Laplace parameter; $\bar{C}_k$, Laplace transform of cell outlet fluid concentration; $\bar{C}_{k-1}$, Laplace transform of cell inlet fluid concentration; t_m, advection characteristic time calculated from:

$$t_m = \frac{\varepsilon V}{Q} \tag{8}$$

For J mixing cells in series, the global transfer function is $G(s)$:

$$G(s) = \frac{\bar{C}_J}{\bar{C}_0} = \left[1 + \frac{t_m s\left(1 + K'_d\right)}{J}\right]^{-J} \tag{9}$$

where $\bar{C}_J$ is Laplace transform of column outlet concentration; $\bar{C}_0$, Laplace transform of column inlet concentration.

Breakthrough moments are given by Van Der Laan relation[20]:

$$\mu_i = (-1)^i \frac{\partial^i G(s)}{\partial s^i}\bigg|_{s=0} \tag{10}$$

The first order moment is:

$$\mu_1 = t_m\left(1 + K'_d\right) \tag{11}$$

The amount $(1 + K'_d)$ is termed retardation factor.

The variance either for water tracer or linearly adsorbed solute:

$$\sigma^2 = \frac{\mu_1^2}{J} \tag{12}$$

Reduced variance for both solutes:

$$\sigma'^2 = \frac{\sigma_r^2}{\mu_1^2} = \frac{\sigma^2}{t_m^2} = \frac{1}{J} \tag{13}$$

Analogy between discrete and continuous approach leads to the following relation[20]:

$$J \approx \frac{\mathrm{Pe}}{2} = \frac{uL}{D_\mathrm{L}} \tag{14}$$

Thus, J is analogous and proportional to the Peclet number. It compares advection to dispersion effects on solute transport. For identical advective conditions, effect of chemical heterogeneity on dispersive behavior of adsorbed solute can be expressed by changing J. This latter will then be the optimization parameter in simulation.

Heterogeneous media experiments

Columns with variable lengths from 5 to 7 cm are packed with granular media of homogeneous size distribution, but with variable activity. Column characteristics are showed in Table 1. Media are made of two types of grains, active and nonactive. Proportion of active grain number indicates medium chemical heterogeneity degree. The less it is, the more heterogeneous the medium is and vice-versa. Active grains are prepared according to a liquid–liquid chromatography technique. Particles of porous chromosorb are impregnated with some quantity of heptamethylnonane oil (HMN). The HMN is the actual adsorbent phase. Hence, active grains contain only one type of active sites. Use of these systems allows variation of chemical heterogeneity by varying active grains number and so varying the HMN amount on one grain without varying the global HMN amount into the medium. Consequently, comparison between behaviors of adsorbed solute on the set of columns can be accomplished at constant medium global capacity. So, media activity is variable at the aggregate scale. Then, chemical heterogeneity is as important as hydrodynamic dispersivity. Inert grains consist of quartz sand. Chemical heterogeneity scale is related to the mean number proportion of active grains, γ. It is calculated by the ratio of active grains number to the total grains number. So γ is the probability for a fluid molecule to meet an active grain. The more important it is, the less heterogeneous the medium is. So, chemical heterogeneity scale is proportional to $1/\gamma$. This latter will be the considered as the heterogeneity parameter in experiment analysis. Solution of calcium chlorides is used either as permanent fluid in flow or as water tracer. Adsorption consists of linear partition of toluene between aqueous solution and HMN according to following expression:

$$S = 78.85 \times C \tag{15}$$

where S is toluene concentration in adsorbed phase, [mol/kg HMN]; C, toluene initial concentration in liquid phase, [mol/cm^3]. Table 2 shows used solutions. Breakthrough curves of either water tracer or toluene will be plotted according to time to respective first order moment ratio. Breakthroughs spreading will be expressed in terms of reduced variance.

Table 2. Tracing Solutions

Permanent fluid	$CaCl_2$, 10 mol/m^3
Water tracer	$CaCl_2$, 20 mol/m^3
Adsorbed solute	Toluene at 10% of water solubility at 25°C

Results and Discussion

Experimental results

Experiments have been performed at local equilibrium condition at 0.0167 cm^3/s flow rate. Breakthrough curves for water tracer are superimposed as shown in Figure 1. Very close values are obtained for reduced variances for both columns (between 0.102 and 0.108), unless the column number 4, which is shorter than the others. Also, breakthrough curves are symmetric and t/μ_1 corresponds for both $C/C_0 \approx 0.5$. So, packing is well accomplished and there are no zones of stagnant fluid exchanging solute with mobile phase. This confirms validity of local equilibrium assumption. Dispersion is only because of hydrodynamic dispersivity. However, toluene breakthrough curves (Figure 2) are more spread than water tracer ones, whereas according to predictions of linear chromatography theory, they should be superimposed. Also, unlike water tracer curves, they are asymmetric and t/μ_1 corresponds to C/C_0 greater than 0.5. Toluene curves look like as in the case of internal diffusion limitation. However, active grains are microporous and should not allow fluid phase diffusion of adsorbed solute. Diffusion into HMN may occur, but in this case, time diffusion must depend on HMN amount on the grain and cause important variations in mean residence time. As only active grain number varies, increased toluene breakthrough curve spreading is because of media chemical heterogeneity variation. Spreading is increased, as active grains are rare. It seems in fact that important mobile fluid concentration gradients are created because of important variation of HMN distribution, although a constant global amount of HMN. This affects toluene plume global dispersion. Variation of toluene-reduced variance with chemical heterogeneity scale is linear as shown in Figure 3 and the following fitting equation:

$$\sigma_r'^2 = 0.097\frac{1}{\gamma} + 0.024 \qquad (16)$$

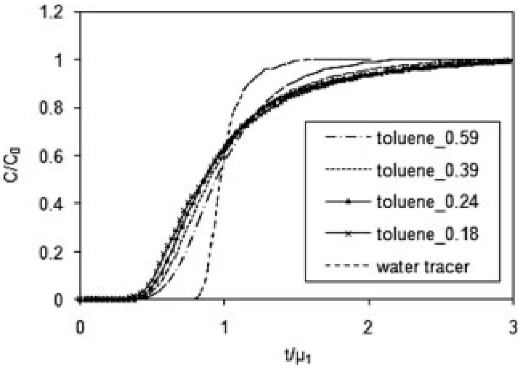

Figure 2. Toluene breakthrough curves compared with the water tracer one at different chemical heterogeneities.

According to this equation, if the medium is homogeneous, i.e., γ is equal to 1, $\sigma_r'^2$ is about 0.101. This value is close to σ'^2 for water tracer, as predicted by the linear chromatography theory. As γ varies from 0 to 1, the chemical heterogeneity scale varies from 1 to 8. The value of $\sigma_r'^2$ at the origin and for γ below 1 has no physical meaning. This should not be the case for the slope. But, till now, there is no information about the meaning of the slope. However, as medium capacity has been kept constant, it may be related to the slope. By analogy with hydrodynamic dispersivity, a chemical activity dispersivity, α_L', proportional to $L \times \sigma_r'^2$, is defined in order to avoid medium length effect on $\sigma_r'^2$ and is plotted vs. the chemical heterogeneity scale. Results corresponding to the hydrodynamic dispersivity are fitted by their mean value ($\approx$0.73 cm) with tolerated error range of 5% (Figure 4). Those corresponding to activity dispersivity show two distinguished zones (Figure 4): the first one for $1/\gamma \leq 3.5$ ($\gamma \geq 0.32$) where dispersivity evolution is linear, and the second zone for $1/\gamma > 3.5$ ($\gamma < 0.32$) where dispersivity seems to achieve a limit value. This behavior means that the activity dispersivity is greater than the hydrodynamic one and is not only related to grain size distribution but depends also on the chemical heterogeneity scale. Chemical activity dispersivity seems to be the dominant heterogeneity scale and behaves as the hydrodynamic one that numerical values

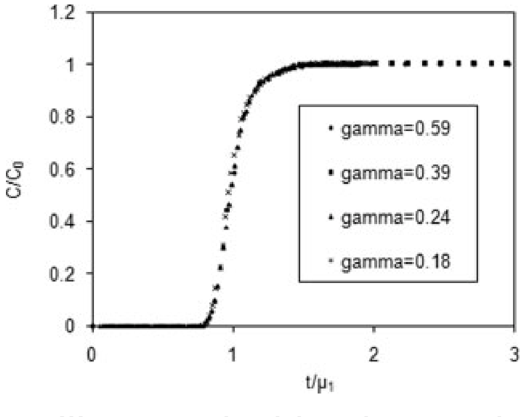

Figure 1. Water tracer breakthrough curves obtained for different chemical heterogeneities.

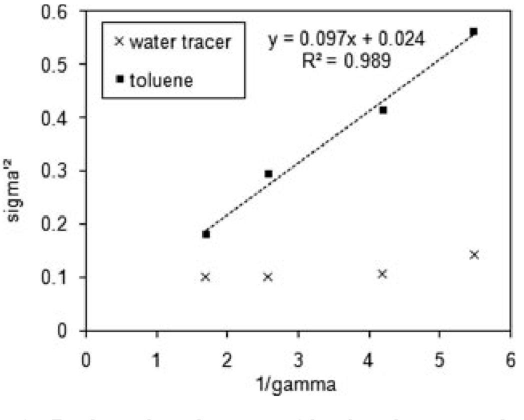

Figure 3. Reduced variances of both toluene and water tracer at different chemical heterogeneities.

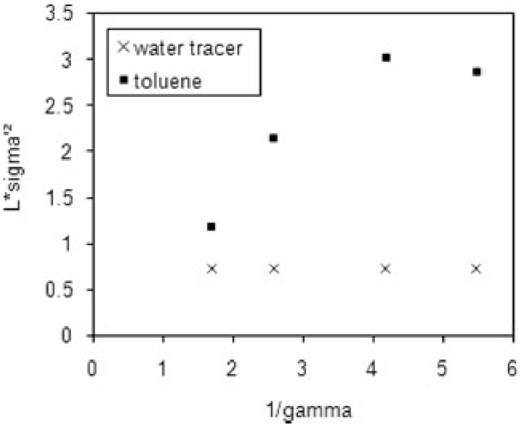

Figure 4. Chemical activity dispersivity vs. chemical heterogeneity.

correlate with the scale of the experiment.[1,15,16,21,22] So, chemical activity dispersivity seems also to be scale-dependent as it has quickly achieved a limit value. In fact, although active grain number has been changed from a medium to another, the actual chemical heterogeneity scale seems to be very slightly varied. Chemical activity dispersivity notion is useful for modeling solute transport into heterogeneous media. According to experimental observations, one can imagine that a linearly adsorbed solute behaves into a chemically heterogeneous medium as it does into a homogeneous one but with greater dispersivity. In this case, effective parameters for adsorbed solute are also related to the breakthrough spreading as in an actual homogeneous medium. Such heterogeneous medium is termed pseudo-homogeneous. As $\sigma_r'^2 > \sigma'^2$, one can define a toluene effective dispersion coefficient in pseudo-homogeneous medium D'_{Lr} such $D'_{Lr} > D_{Lr}$ and related to reduced variance by:

$$\sigma_r'^2 = \frac{2D'_{Lr}}{u_r L} \tag{17}$$

Dividing effective parameters by a constant retardation factor gives a new longitudinal dispersion coefficient D'_L greater than hydrodynamic dispersion coefficient D_L.

To check validity of assumption of dominant heterogeneity consisting of activity dispersivity, the mixing cells in series model is used to simulate the experimental breakthrough curves.

Toluene breakthrough simulations

The basis of the discrete method applied to transport into pseudo-homogeneous media is that hydrodynamic dispersivity is no longer dominant and should be replaced by chemical activity dispersivity. When the medium is chemically homogeneous, i.e., as long as the chemical heterogeneity scale is smaller than the mixing length, the theoretical stage consists of a mixing cell that size is equal to L/J. Linearly adsorbed solute dispersion is controlled only by hydrodynamic dispersion. However, if the chemical heterogeneity scale is as greater as or greater than the mixing length, the theoretical stage size should be superior to L/J. So, a smaller number of theoretical stages than J is needed. The new number, noted J', determines the new dominant heterogeneity scale L/J' or the new dispersivity. Mass balance into a theoretical stage is written such in a homogeneous medium but with different parameters:

$$QC_{k-1} = QC_k + \frac{\varepsilon V}{J'}\frac{dC_k}{dt} + \frac{(1-\varepsilon)V}{J'}\frac{d\langle C_{p,k}\rangle}{dt} \tag{18}$$

where $\langle C_p \rangle$ is mean solid volume concentration.

This model considers a mean concentration in solid phase, so a mean global distribution coefficient, K'_d, is used. This is compatible with experiments where global capacity has been kept constant.

$$K'_d = \frac{1-\varepsilon}{\varepsilon}\rho'_a K_d \tag{19}$$

$$\rho'_a = \frac{M_{HMN}}{V} \tag{20}$$

M_{HMN} is medium total HMN mass.

Hence:

$$QC_{k-1} = QC_k + \frac{\varepsilon V}{J'}\frac{dC_k}{dt} + \frac{V}{J'}K'_d\frac{dC_k}{dt} \tag{21}$$

Medium transfer function is:

$$G(s) = \frac{\bar{C}_{J'}}{\bar{C}_0} = \left[1 + \frac{t_m s(1+K'_d)}{J'}\right]^{-J'} \tag{22}$$

Breakthrough moments are calculated from Van Der Laan relation:

$$\mu_1 = t_m(1+K'_d) \tag{23}$$

$$\sigma_r'^2 = \frac{1}{J'} \tag{24}$$

Hence:

$$D'_L = \frac{uL}{2J'} \tag{25}$$

As explained above, as J' is smaller than J, D'_L is greater than the hydrodynamic dispersion coefficient D_L. From the first-order moment, it appears that there is no effect of chemical heterogeneity on the mean residence time of adsorbed solute. It only depends on the advection characteristic time and medium global capacity. This result is confirmed by experimental toluene breakthroughs crossing each other for $t/\mu_1 = 1$ at about the same C/C_0 (Figure 1). However, reduced variance is directly related to the new number of heterogeneous stages, and thus is implicitly related to the chemical heterogeneity scale. Simulation of toluene breakthrough curves on heterogeneous media is accomplished by optimization of J', and consequently by optimization of D'_L. Values of longitudinal dispersion coefficients are given in Table 3. From Figures 5–8, good agreement between modeling results and experimental data are obtained. It means that imagination of a pseudo-homogeneous medium with greater dispersivity than hydrodynamic one seems to be a good approximation of

Table 3. Longitudinal Dispersion Coefficients Calculated from Toluene Transport Simulations

g	D_L (cm^2 s^{-1})	D'_L (cm^2 s^{-1})
0.59	0.014	0.021
0.39	0.016	0.036
0.24	0.016	0.050
0.18	0.015	0.051

linearly adsorbed solutes transport into chemically heterogeneous media. Although assumption of supplementary concentration gradients means that local capacity may affect relation between heterogeneity and global dispersion, the pseudo-homogeneous simulation considers these gradients globally as it is made in homogeneous media for hydrodynamic dispersion. Note however, simulations provide quite symmetric curves, unlike experiments. One can observe a faster breakthrough for simulated curves than the experimental ones. This is only because of the symmetric character of the pseudo-homogeneous model as predicted by Eq. 24. Accomplished simulation purpose was to show how chemical heterogeneity can affect transport parameter at column scale, and thus the efficiency of a fixed bed adsorption process. However, explicit relation between chemical heterogeneity and solutes' global dispersion is needed in order to give a meaning to the slope in Eq. (16) and the observed asymmetry.

Summary and Conclusion

This article aimed at showing, measuring, and modeling effect of medium chemical heterogeneity on global dispersion of a linearly adsorbed solute at column scale. Chemically heterogeneous media have been prepared so that chemical heterogeneity scale variation has been easily measured and controlled. Active grains have been mixed to inert ones. Global capacity of media has been kept constant whereas local capacity has been varied in proportion to the variations in active grains number. Heterogeneity scale has been quantified by the inverse of active grains number ratio to total grains number. This ratio is similar to the probability for a fluid molecule in flow to meet an active grain. Hence, the most numerous the active grains were, the less heterogeneous the medium was. The chemical heterogeneity scale was about few grains mean diameter of magnitude, it was then as important as the hydrodynamic dispersivity. Hydrodynamic properties of all media were identical. Breakthrough curves of adsorbed solute showed a visible effect of chemical heterogeneity on global solute plume dispersion increasing. The more heterogeneous the medium was, the more spread the adsorbed solute breakthrough was. Reduced variance showed a linear variation with chemical heterogeneity scale. Chemical activity dispersivity has been defined by analogy with the hydrodynamic one. The activity dispersivity showed an early linear evolution with chemical heterogeneity but seemed to reach a limit value. This behavior is analogous to the hydrodynamic dispersivity one, which varies till achieving a limit value corresponding to the ERV for a sample dimension. So, the adsorbed solute into chemically heterogeneous media seemed to be identical to transport into a homogeneous one considering the different dispersive properties. Using analogy between the continuous approach and the mixing cells in series one, a pseudo-homogeneous discrete model has been developed to simulate experimental breakthroughs on hetero-

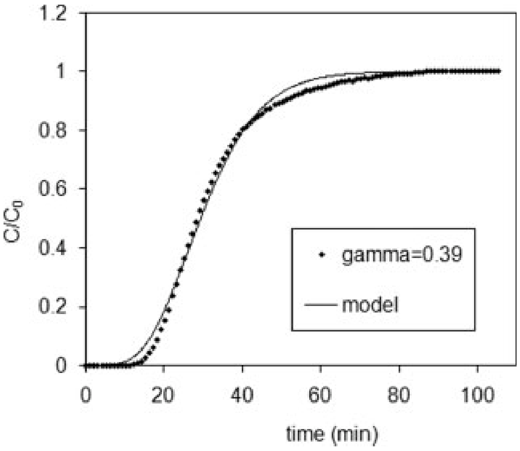

Figure 6. Simulation of toluene breakthrough curve with pseudo-homogeneous model, γ = 0.39.

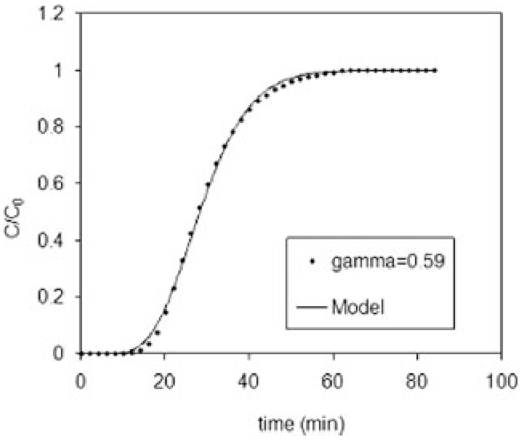

Figure 5. Simulation of toluene breakthrough curve with pseudo-homogeneous model, γ = 0.59.

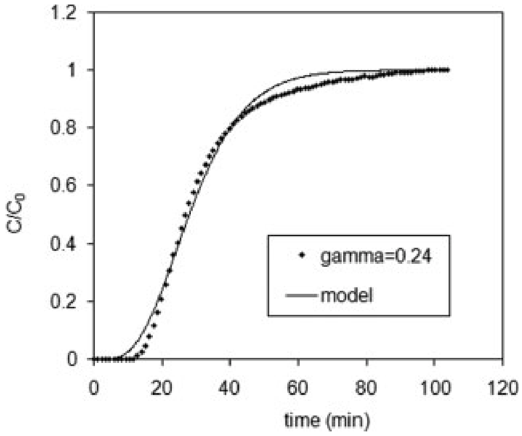

Figure 7. Simulation of toluene breakthrough curve with pseudo-homogeneous model, γ = 0.24.

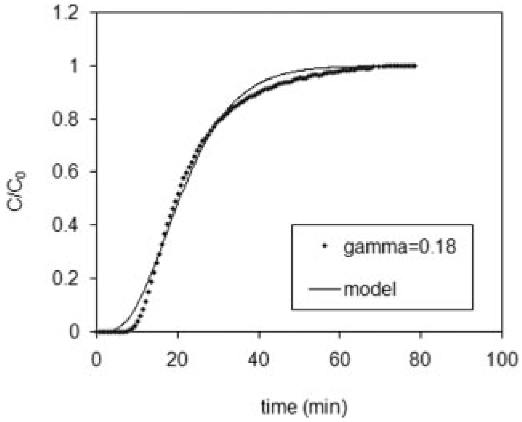

Figure 8. Simulation of toluene breakthrough curve with pseudo-homogeneous model, $\gamma = 0.18$.

geneous media. The model considered a greater cell volume than in the case of hydrodynamics or homogeneous medium. A greater cell means a greater mixing length than hydrodynamic value, and hence a greater global longitudinal dispersion coefficient than the hydrodynamic dispersion coefficient. Simulation of experimental curves needed optimization of dispersion parameter. The pseudo-homogeneous model gave coherent results with experimental data and results of optimization showed in fact a greater longitudinal global dispersion coefficient than the hydrodynamic one, and which was growing till achieving a limit value. Perspectives are to develop a detailed model based on the discrete approach that provides an explicit relation between dispersion and chemical heterogeneity respective parameters. The model would give a physical meaning to the coefficients given in Eq. 16.

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