Effect of Chemical Heterogeneity on Linear Adsorbed Solute Dispersion in fixed bed

K. Kaabeche-Djerafi\textsuperscript{a*}, S. Semra\textsuperscript{b}, N. Bendjaballah-Lalaoui\textsuperscript{c}

\textsuperscript{a*} Department of Industrial Chemistry, University Mentouri of Constantine (UMC), BP 325, Route Ain El Bey, Laboratory Pollution Water Treatment (LPTE), 25017 Constantine, Algeria (E-mail: kaabeche_khatima@yahoo.fr)

\textsuperscript{b} Department of Industrial Chemistry, University Mentouri of Constantine (UMC), BP 325, Route Ain El Bey, 25017 Constantine, Algeria (E-mail: safia.semra@yahoo.fr)

\textsuperscript{c} Department of Industrial Chemistry, University Houari Boumediène of Sciences and Technology (USTHB), BP 32 El Alia, 16111 Laboratory Materials technology (LTM) Bab Ezzouar, Algiers, Algeria (E-mail: nadia_bendjaballah@yahoo.fr)

Abstract

The paper aims at investigating the importance of including chemical heterogeneity in fixed bed as it has been found to induce additional dispersion. A discrete chemical heterogeneity distribution has been considered in the one-dimensional advective-dispersive equation. The partial differential equation was solved using finite volumes method based on the Adam-Bashforth algorithm. Increased dispersion was estimated comparing breakthrough curves second order moments keeping identical hydrodynamic properties as well as medium global capacity. In the objective to prove the presence of chemical heterogeneity effect, we study in the first the transport in homogeneous and chemically heterogeneous medium without hydrodynamic dispersion. Then effect of medium capacity on linear adsorbed solute dispersion into chemically heterogeneous at constant bed length and at the same chemical heterogeneity distribution was investigated. After that, different distributions were considered at different bed lengths too. Effect of chemical heterogeneity was found has nonregular behavior with the medium size but depending on the distribution type though a constant mean value of the distribution. As a result, dispersion increase due to chemical heterogeneity which depends essentially on the column size and on the nature of heterogeneity distribution causing dependence of the breakpoint time on both.

Keywords: adsorption; chemical heterogeneity; dispersion; fixed bed; porous media.
1. Introduction

Scale-up involves answering the technical question, "How will this function on a larger scale?" The precise function of scale-up is that the process development at large scale should achieve the same conversion, yields and selectivities, and, in some cases, possibly improve the results [1]-[2]. When processes are transferred from the laboratory or pilot scale to the commercial one, many parameters should be taken into account in particular if the corresponding phenomena depend on the system size. In the case of adsorption and ion exchange in fixed beds, the scale-up mainly takes into account mass transfer phenomena and of course the column hydrodynamics. Under specific conditions, the similarity rules can be drawn using the continuity equation, the rates equations, and/or the hydraulic equation. One of the scaling parameters is the contact time, $\tau$. It defined by [3].

$$\tau = \frac{eV}{Q_{rel}} = \frac{LE}{U}$$

(1)

Where $Q_{rel}$ is the relative volumetric flow rate, commonly expressed in empty bed volumes per hour; $Q$ is the operating flow rate; $e$, bed porosity; $L$, bed length; $U$, linear velocity.

It is clear that for the same ion-exchange or adsorption system, the same inlet fluid concentration and solid capacity at saturation, the exit fluid concentration at each time interval $t$ will be the same for bed size provided that particle size and other parameters are invariant from laboratory scale ($LS$) to full one ($FS$). In this case, the scale up rule is:

$$\tau_{FS} = \tau_{LS} \Leftrightarrow \left( \frac{LE}{U} \right)_{FS} = \left( \frac{LE}{U} \right)_{LS}$$

(2)

If the scale up is based on the contact time, the results obtained from the laboratory scale can be directly used in the large one and the performance of the bed can be accurately evaluated. Consequently, if we have a contact time-breakpoint volume relationship derived from the laboratory bed experiments, we can use this relationship to evaluate the breakpoint volume of the large-scale unit for the specified contact time [3]. However, it is important to notice that the usually used equation of continuity does not consider any kind of adsorbent chemical activity distribution. This latter seems in fact to be determinant in solutes behaviour into fixed beds [4].

It has been found that the obtained breakthrough curve is more spread than the one expected neglecting heterogeneity. Hence, the obtained breakpoint time ignoring is earlier than the expected one. This may induce an overestimation of the necessary contact time which implies higher concentration at the breakthrough than desired for the same scale as shown in figure 1.
Actually, as known in solutes transport in groundwater literature, effect of chemical heterogeneity, if exists, vanishes at long distances from the inlet [5]-[6]. Yet, these "long distances from the inlet" have to be precisely determined as they have to be compared to the chemical heterogeneity scale. Consequently, one should identify how a well known and measurable chemical heterogeneity affects breakthrough curves spreading at different scales and thus how this affects the scaling based on the contact time. This paper aims at introducing the chemical heterogeneity in the continuity equation and to show its effect at laboratory and pilot scales.

2. Transport modeling in the presence of chemical heterogeneity

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 $l_2$ (Fig 2).

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

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

(3)
The mean value of the distribution is \( \gamma \) defined by
\[
\gamma = \frac{l_1}{l_1 + l_2}
\] (4)

The continuity equation (the advection-dispersion equation) is written such
\[
U \frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} + \frac{1 - \varepsilon}{\varepsilon} \frac{\partial q}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2}
\] (5)

Where \( U \) is the linear flow velocity; \( C \) is the fluid concentration; \( q \) is the solid phase concentration; and \( D_L \) is the dispersion coefficient. Considering a linearly adsorbed solute under equilibrium conditions, the solid phase concentration is
\[
q(x,t) = \rho_p K_d C(x,t) \Gamma(x)
\] (6)

Where \( K_d \) is the thermodynamic distribution coefficient, constant for linear adsorption, \( \rho_p \) is the bulk density. Using the following dimensionless variables
\[
T = t/t_0 ; t_0 = \varepsilon V/Q ; X = x/d_p ; C^* = C/C_0 ; \alpha = d_p U/t_0 ; \beta = D_L/d_p U
\]

where \( t_0 \) and \( d_p \) are respectively the mean fluid passage time (or the advection characteristic time) and the particle mean size, the adsorbed equation becomes:
\[
\frac{\partial C^*}{\partial X} + \alpha \left( 1 + \Gamma(X) \rho_p K_d \frac{1 - \varepsilon}{\varepsilon} \right) \frac{\partial C^*}{\partial T} = \beta \frac{\partial^2 C^*}{\partial X^2}
\] (7)

The dimensionless equation has solved using the finite volumes method according the Second Order Backward and using the Adam Bashforth scheme [7].

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
\[
\left( \frac{\partial C}{\partial X} \right)_{X=0} = 0 \text{ at the outlet.}
\]

The effect of chemical heterogeneity 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 [4]. 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 [8], the breakthrough curves spreading is accounted for by the second order central moment \( \sigma^2 \) and the reduced variance \( \sigma^2' \), given by:
\[
\sigma^2 = \int_0^\infty 2t(1 - C^*(t))dt - \mu_1^2
\]  

The reduced variance, \(\sigma^2\) accounts for solute effective dispersion and is calculated by:

\[
\sigma^2 = \frac{\sigma^2}{\mu_1^2}
\]

Where \(\mu_1\) is the mean retention time. It is directly related to the medium mean capacity \(K'd\) and the advection characteristic time by (Sardin, 1993)

\[
\mu_i = \int_0^\infty (1 - C^*(t))dt \text{ or } \mu_i = \int_0^\infty (1 + K_d')
\]

The medium mean capacity, said also the dimensionless distribution coefficient, is function of the mean probability of activity distribution via \(K' = \gamma \frac{1 - \epsilon}{\epsilon} \rho_p K_d\)

So, breakthrough curves are exploited plotting \(\sigma^2/\sigma^2_w\) versus \(1/\gamma\) where \(\sigma^2_w\) 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 \(\sigma^2/\sigma^2_w\) 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, effect of chemical heterogeneity was evaluated comparing chemically homogeneous medium with chemically heterogeneous medium. After that, different medium capacity at constant bed length and constant active layer thickness were investigated then different distributions were considered for constant bed length. Model constant parameters are: \(Q = 1.66 \times 10^{-8} \text{ m}^3/\text{s}; d_p = 4 \times 10^{-6} \text{ m}; \rho_p = 2600 \text{ kg/m}^3; \epsilon = 0.48\). The dispersion coefficient considered is equal to the hydrodynamic one and calculated according to \(D_L = 4 \frac{d_p U}{10}\).

### 3. Results and discussion

#### 3.1 Demonstration of the existence of chemical heterogeneity

In the first investigation we consider only the advective transport in the absence of hydrodynamic dispersion, \(D_L = 0\), for chemical homogeneous and chemical heterogeneous medium (at a constant mean value of the distribution, \(\gamma = 0.148\)). Equation (5) for advective transport of a single solute becomes as follows:

\[
\frac{\partial C^*}{\partial X} + \alpha \left(1 + \Gamma(X) \frac{1 - \epsilon}{\epsilon} K_d \right) \frac{\partial C^*}{\partial T} = 0
\]

The solution of this equation gives the distribution of retention time (DTR), breakthrough curves under the assumption of local equilibrium and in the absence of hydrodynamic dispersion were shown in the following figure 3 on both chemical homogeneous and chemical heterogeneous medium.
The fact that we have divided by $\mu_1$ this means that the interaction was removed, and the gap between homogeneous and chemical heterogeneous represents the effect of chemical heterogeneity. Subsequently we present the influence of some parameters on the chemical heterogeneity.

3.2 Influence of medium capacity $K'_d$ on the global dispersion

The influence of medium capacity on linear adsorbed solute dispersion into chemically heterogeneous fixed beds at constant bed length $L=0.4$ m and constant active layer thickness $l_1 = 0.02$ m is investigated. Breakthrough curves are exploited plotting $\sigma^2/\sigma^2_w$ versus $1/\gamma$ where $\sigma^2_w$ corresponds to a water tracer breakthrough curve spreading as is mentioned above was shown in figure 4.
Dispersion due to chemical heterogeneity shows a linear increase. In addition, unlike homogeneous media ($1/\gamma = 1$) for which $\sigma'^2/\sigma_w'^2 = 1$ whatever $K'_d$ is, the medium capacity seems to influence this ratio for chemically heterogeneous ones. Moreover, one notice an increase of the slope by enhancing $K'_d$ from 1 to 100. As said by [4], medium activity variability implies solute adsorbability variability, creating fluid phase concentration gradients which lead in turn to an additional dispersion this result is according with [11]. Consequently, the more favorable the adsorption is (high medium capacity), the greater the fluid concentration gradients are and, hence, the greater dispersion increase is.

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 nonnative 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.

3.3 Effect of the distribution $\Gamma(x)$

In this section, the effect of chemical heterogeneity distribution was investigated keeping a constant $K'_d$, and varying the active and non active layer thickness for the same mean probability $\gamma$. The effect of chemical heterogeneity on breakthrough spreading is shown in figure 3 for five different bed lengths according to a ratio $l/L$ varying from 0.03 to 0.15. Results show again a linear increase of the breakthrough spreading with the heterogeneity scale. For a specific length, the thicker the active layer is, the greater the slope is. However, nonregular effect of medium scale on the relation between heterogeneity and dispersion is not clear yet.
One can imagine that for the same \( \gamma \), the greater \( l_1 \) is, the greater the differences between fluid concentration zones are and thus the greater the additional dispersion is. Inversely, when layers are too thin, their number is great and medium approaches a homogeneous one. This leads to lower dispersion.

4. Conclusion

Investigation of chemical heterogeneity effect on the breakthrough curve spreading has been simulating in order to show, on one hand, the effect of medium capacity, on the other hand, the influence of the heterogeneity distribution. Results showed a perceptible difference of the effect of chemical heterogeneity from the small to the larger scale. 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, the contact time obtained from the same chemically heterogeneous medium at small scale can no longer be kept constant when transferring to a large unit as the heterogeneity effect decreases with the medium size. In fact, the contact time would be underestimated and the operation would be stopped earlier than it should.

References


