



# Decreased peak tailing during transport of solutes in porous media with alternate adsorption properties

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## HIGHLIGHTS

- Spatial alternation of Langmuir and Anti-Langmuir adsorption zones reduces concentration overloading related band widening.
- Peak widening reduction is due to alternation of frontal and rear sharpening in the Langmuir and Anti-Langmuir zones.
- Efficiency of the Langmuir-Anti Langmuir alternation varies with details of the spatial adsorption geometry.
- A strategy to reduce peak broadening has been developed.

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## ABSTRACT

In adsorption based separation techniques or in environmental applications where adsorption on a porous matrix is involved, the broadening of migrating bands of solutes varies with the characteristics of the adsorption isotherms and is generally overwhelming at solute concentrations deep in the non-linear region. We introduce here a novel concept to minimize concentration overloading dispersion: We show theoretically that a spatial alternation of Langmuir (L) and Anti-Langmuir (AL) zones along the displacement direction induces an accordion effect, i.e. an alternation of sharpening and dilution of the solute zones, reducing in the end the final broadening of the peak. We quantify in the parameter space of the problem the reduction in concentration overloading related band widening of the L-AL system compared to the pure L or AL cases. A numerical analysis of the solute transport reveals a dependence of solute spreading on the ratio of sample to stationary phase zone widths and on the intensity of the adsorption parameter. The initial position of the sample solvent in its surrounding liquid i.e. whether the displacement starts in a L or AL zone is also shown to have an influence on the dispersive behavior. An analysis is performed to highlight the optimal alternance geometry to minimize solute spreading.

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## 1. Introduction

In porous media, understanding the transport of solutes that can adsorb on the porous matrix is of importance for environmental applications as, for instance, in carbon capture and sequestration (Metz et al., 2005), oil recovery (Farajzadeh et al., 2012) or contaminant remediation in subsurface systems (Lüehrmann et al., 1998; Abriola, 1987). In chemical and pharmaceutical engineering, processes such as chromatographic separation of solutes from a mixture also exploit transport and adsorption in porous systems to obtain high purity compounds (Nicoud et al., 2015; Guiochon et al., 2006). Such techniques often require multi-component separation, an initial as high as possible concentration

is desired to avoid further costly or even analyte degrading steps to remove the solvent.

In the above applications, the solutes present in a given liquid sample displaced by a miscible displacing fluid in the porous matrix can be retained on the solid phase following the reversible adsorption-desorption step (Ruthven et al., 1984)

$$A_m \frac{k_a}{k_d} A_s. \quad (1)$$

Here,  $A_m$  and  $A_s$  represent the solute molecules in the mobile and stationary phases respectively, where their concentrations are equal to  $c_m$  and  $c_s$ , while  $k_a$  and  $k_d$  are the adsorption and desorption kinetic constants. During the displacement, the solutes are progressively separated because of a selective adsorption of the components on the porous matrix while dispersion causes broadening of the solute bands (Ruthven et al., 1984; Nicoud et al., 2015). In this

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context, a general goal of the applications mentioned above is to minimize this concentration overloading related band widening.

The spreading of solutes in a porous matrix is dependent on the adsorption isotherm  $c_s = f(c_m)$  expressing the dependence of the solute concentration in the stationary phase  $c_s$  on its concentration in the mobile phase  $c_m$  (Guiochon et al., 2006; De Vault, 1943). For the linear adsorption isotherm,  $c_s = Kc_m$ , where  $K = k_a/k_d$  is the equilibrium constant of the adsorption–desorption processes. The solute retention is then characterized by the retention factor  $k = FK$ , where  $F = V_s/V_m = (1 - \epsilon_{tot})/\epsilon_{tot}$  is the phase ratio of the volume  $V_s$  and  $V_m$  of the stationary and mobile phases, where  $\epsilon_{tot}$  is the total porosity or void volume fraction of the porous medium. When the hydrodynamic dispersion and mass transfer limitations are not strong, the linear isotherms result in symmetric solute profiles (see Fig. 1). They can typically be used only if the amount of solutes in the sample is sufficiently low (Rhee et al., 1986; Rhee et al., 1989). In numerous applications however, the concentration of a component in the stationary phase at equilibrium depends nonlinearly on its concentration in the mobile phase (Gritti and Guiochon, 2005). For a monolayer adsorption, the simplest nonlinear adsorption models are given by Langmuir and anti-Langmuir adsorption isotherms (Giles et al., 1974). Equilibrium theory is an elegant approach to investigate dynamic behavior in chromatography. As it is often justified to assume thermodynamic equilibrium between the mobile and the stationary phase, the governing equations that describe analyte transport can often be appropriately expressed as a system of hyperbolic first-order partial differential equations (Rhee et al., 1986; Rhee et al., 1989; Mazzotti, 2006; Ortner et al., 2014).

### 1.0.1. Langmuir isotherm

The Langmuir isotherm assumes that, on the porous matrix, there is only a fixed number of sites on which the molecules can adsorb and that these molecules do not interact with the neighbouring sites. The amount of solute needed to saturate the stationary phase in the column thus depends on the nature of the porous matrix and fixes the saturation capacity of the stationary phase reached when all sites are occupied. The corresponding Langmuir isotherm is expressed as (Giles et al., 1974):

$$c_s = \frac{Kc_m}{1 + b_L c_m}, \quad (2)$$

where  $K$  is the initial slope of the isotherm,  $b_L$  is a term related to the adsorption energy;  $K/b_L = c_{sat}$  is the monolayer capacity. Because of this nonlinear adsorption, the velocity of the solute propagation in the mobile phase increases with  $c_m$ . This is due to the fact that, when all the adsorption sites are occupied at a suffi-

ciently high concentration, the non-retained solutes at the area of local saturation migrate with a narrow velocity distribution (related to the parabolic flow profile) around the unretained velocity of the mobile phase. Meanwhile the upstream retained solutes experience a much broader distribution of velocities around the average retained velocity as a consequence of the continuous switching between the adsorbed and desorbed states. As a result, a shock layer (SL) forms in the course of time at the frontal interface of the peak (Rhee et al., 1986; Rhee et al., 1989). This SL is a thin region of space where the concentration varies continuously but rapidly, and that propagates as a constant pattern (Whitham, 1957). At the rear interface, on the other hand, a rarefaction wave (RF) corresponding to an expanding wave is formed (Helfferich et al., 1993) (see Fig. 1). On the long term, these two nonlinear waves end up interacting with each other to form an asymptotic triangular peak with a SL at the front, which is a peculiar feature of the Langmuir adsorption isotherm (Guiochon et al., 2006; Rana et al., 2018).

### 1.0.2. Anti-Langmuir isotherm

The anti-Langmuir isotherm is observed in presence of adsorbate–adsorbate interactions favoring further adsorption (Cavazzini et al., 2002; Golshan-Shirazi and Guiochon, 1989). Such a cooperativity overloading effect induces an adsorption curve opposite to that of the Langmuir isotherm i.e.  $c_s$  increases more rapidly with an increase in  $c_m$  (Fig. 1). The anti-Langmuir adsorption isotherm is expressed as

$$c_s = \frac{Kc_m}{1 - b_{AL} c_m}, \quad (3)$$

where  $b_{AL}$  is the adsorption parameter. This isotherm is valid provided  $c_m < c_{th} = 1/b_{AL}$  where  $c_{th}$  corresponds to the threshold concentration of the column. Because of the increased adsorption at larger  $c_m$ , the velocity of the solute in the mobile phase is smaller in the zones of larger concentrations, which results in the formation of a SL at the rear interface and of a RF wave at the frontal interface (Lin et al., 1995; Rana et al., 2019). Anti-Langmuir isotherms feature therefore asymptotic triangular peaks with a SL at the back (see Fig. 1).

The Langmuir (L) or Anti-Langmuir (AL) models give an appropriate representation of the adsorbed behaviour in many systems (Mazzotti, 2006). Because of the nonlinear adsorption properties, the tailing at either the rear (L) or frontal (AL) part of the spatial concentration profile enhances the concentration overloading related band widening and thus impairs the resolution of solute separation or the efficiency of pollution remediation or instance. Efforts are thus being developed to eliminate or reduce the peak tailing effects (Meyer, 2010). Alternatively, sharpening of the sample band by applying solvent of modifier gradients is a well-known approach to reduce the sample band width (Strong and Frey, 1997).

In this context, our aim in the present study is to propose and study theoretically a heterogeneous configuration with multi-site adsorption to analyze the conditions on the geometry and adsorption properties of the porous matrix to reduce the solute spreading at overloading concentrations. Specifically, we show that an alternation along the displacement of zones with L or AL adsorption properties can decrease the broadening of peaks thanks to the succession of sharpening of the solute spatial concentration profile at the front or at the rear depending whether the sample crosses a L or an AL zone.

## 2. Langmuir/Anti-Langmuir (L-AL) adsorption model

We consider a heterogeneous porous matrix consisting of an alternation along the displacement direction  $x$  of zones with

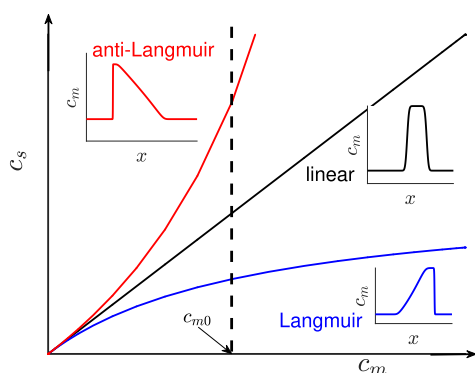


Fig. 1. Linear, Langmuir and Anti-Langmuir isotherms with their typical corresponding peak shapes.

different adsorption properties. In some zones, the adsorption on the surface is described by a classical Langmuir isotherm (Eq. (2)) while the adsorption on the complementary zones of the surface follows an anti-Langmuir isotherm (Eq. (3)) behavior. The porous matrix is thus composed of alternating bands of two types of sites characterized by different adsorption isotherms. The sites are supposed to behave independently. This is possible for instance when a component like butylbenzene is subject to weak forces of a polar stationary phase. The aromatic analyte-analyte interaction can then dominate, leading to Anti-Langmuir behavior while, in a reverse phase coating, a stronger interaction with the stationary phase will rather give a Langmuir behavior (Gritti et al., 2002; Gritti and Guiochon, 2003; Fornstedt et al., 1999). Our objective is to analyze the influence of this alternation of adsorption properties on the widening of a sample of given initial width  $L$  displaced along this system at a given velocity  $U$ . The flow is assumed to be uniform and the porous matrix is supposed to be radially homogeneous.

### 2.1. L-AL adsorption isotherm

Local adsorption at a position  $x$  and at a time  $t$  is given by the isotherm

$$c_s(x, t) = \frac{Kc_m(x, t)}{1 + b(x)c_m(x, t)}. \quad (4)$$

Depending whether the local site at position  $x$  is of the L or AL type, we use

$$b(x) = \begin{cases} b_L, & \text{if } x \in \text{Langmuir zone,} \\ -b_{AL}, & \text{if } x \in \text{anti - Langmuir zone.} \end{cases} \quad (5)$$

The constant  $b_L$  quantifies the adsorption-desorption in the Langmuir zone while  $b_{AL}$  characterizes the anti-Langmuir sites. As stated before, for the anti-Langmuir isotherm, the function (4) is defined only for  $c_m < 1/b_{AL}$ . We define a non-dimensional parameter  $\delta = b_L/b_{AL}$  as the ratio of the non-linear adsorption parameters of the Langmuir and anti-Langmuir isotherms.

In this study the following simplifying assumptions are made:

- The adsorption surface is divided equally in Langmuir and Anti-Langmuir zones of equal width  $L_{plate}$  covering the column alternatively.
- There is no interaction of the species adsorbed on one type of site with those of the other sites.
- The equilibrium constant  $K$  is the same for all zones.
- The non-linear adsorption parameter  $b_L$  and  $b_{AL}$  of the Langmuir and anti-Langmuir zones are independent of each other and depend on the threshold mobile phase concentration  $c_{th}$  and thus on the porous matrix.

Our objective is to achieve reduced peak tailing and hence find the optimal geometrical and adsorption conditions to reduce the concentration overloading related band widening. We next analyze the spreading dynamics of adsorbed solutes on this heterogeneous surface alternating L and AL sites using numerical simulations of the mass balance transfer equation and L-AL isotherms. We show that, with a suitable choice of parameters, the L-AL system leads to a significant reduction of the solute spreading and can be used to reduce the severe tailing of the concentration profiles.

### 2.2. L-AL flow model

As the flow is uniform and the column is assumed to be radially homogeneous, the model is unidimensional. The mass balance equation for the concentration  $c_m$  of the solute in the mobile phase

and  $c_s$  in the stationary phase in presence of advection at speed  $U$  and dispersion reads:

$$\frac{\partial c_m}{\partial t} + F \frac{\partial c_s}{\partial t} + U \frac{\partial c_m}{\partial x} = D \frac{\partial^2 c_m}{\partial x^2}, \quad (6)$$

A constant linear mobile phase velocity is assumed and therefore the model is limited to diluted systems wherein the volume fraction of the solutes is negligible, where  $D$  is the dispersion coefficient. Taking into account the adsorption isotherm (Eq. (4)) for  $c_s$  and using  $k = FK$ , the mass balance Eq. (6) reduces to

$$\frac{\partial}{\partial t} \left( 1 + \frac{k}{(1 + b(x)c_m(x, t))} \right) c_m(x, t) + U \frac{\partial c_m(x, t)}{\partial x} = D \frac{\partial^2 c_m(x, t)}{\partial x^2}. \quad (7)$$

Let  $L_x$  be the length of the uni-dimensional system such that  $x \in [0, L_x]$  and  $x_{in}$  be the initial position of the rear interface of the sample of width  $W$ . The initial mobile phase concentration  $c_m(x, 0)$  is then assumed to be

$$c_m(x, 0) = \begin{cases} c_{th}/\alpha, & \text{for } x \in [x_{in}, x_{in} + W], \\ 0, & \text{elsewhere,} \end{cases} \quad (8)$$

where  $\alpha > 1$ . The initial concentration is always assumed to be smaller than  $c_{th}$  to avoid the divergence due to anti-Langmuir adsorption. The boundary conditions, imposed on concentration  $c_m(x, t)$  and velocity  $u$  are:

$$u = U, \quad \frac{\partial c_m(x, t)}{\partial x} = 0, \quad \text{at the inlet and the outlet.} \quad (9)$$

Thus, at the boundaries, the velocity  $u$  is set to be equal to the injection velocity  $U$  and a no flux boundary condition is imposed on the mobile phase concentration of the solute.

### 2.3. Non-dimensionalized L-AL flow model

To nondimensionalize the governing equations, the concentration  $c_{th}$  is chosen to non-dimensionalise  $c_m$ ,  $b_L$  and  $b_{AL}$ , while  $U$  is taken as the characteristic velocity. Defining the length scale  $L_c = D/U$  and the time scale  $t_c = D/U^2$ , the non dimensional velocity, length and time are defined as (Homsy, 1987):  $\hat{U} = U/U = 1$ ,  $\hat{x} = x/(D/U)$ ,  $\hat{t} = t/(D/U^2)$  while the non-dimensional concentration and adsorption parameters become

$$\begin{aligned} \hat{c}_m &= c_m/c_{th} \\ \hat{b}_L &= b_L c_{th} = b_L/b_{AL} = \delta, \\ \hat{b}_{AL} &= b_{AL} c_{th} = 1 \\ \hat{c}_s &= c_s/c_{th} = \begin{cases} \frac{K\hat{c}_m}{1 + \delta\hat{c}_m}, & \text{if } x \in \text{Langmuir zone,} \\ \frac{K\hat{c}_m}{1 - \hat{c}_m}, & \text{if } x \in \text{anti - Langmuir zone,} \end{cases} \end{aligned}$$

After implementing the above non-dimensionalisation, the mass balance equation becomes:

$$\frac{\partial}{\partial \hat{t}} \left( 1 + \frac{k}{(1 + \hat{b}(x)\hat{c}_m(x, \hat{t}))} \right) \hat{c}_m(x, \hat{t}) + \frac{\partial \hat{c}_m(x, \hat{t})}{\partial \hat{x}} = \frac{\partial^2 \hat{c}_m(x, \hat{t})}{\partial \hat{x}^2} \quad (10)$$

where,

$$\hat{b}(x) = \begin{cases} \delta, & \text{for } x \in \text{Langmuir zone,} \\ -1, & \text{for } x \in \text{anti - Langmuir zone.} \end{cases} \quad (11)$$

After dropping the hats this can be further simplified and written as:

$$\left( 1 + \frac{k}{(1 + b(x)c_m(x, t))^2} \right) \frac{\partial c_m(x, t)}{\partial t} + \frac{\partial c_m(x, t)}{\partial x} = \frac{\partial^2 c_m(x, t)}{\partial x^2} \quad (12)$$

Defining  $\kappa = \left(1 + \frac{k}{(1+b(x)c_m(x,t))^2}\right)$ , we get finally:

$$\frac{\partial c_m(x,t)}{\partial t} = \frac{1}{\kappa} \frac{\partial^2 c_m(x,t)}{\partial x^2} - \frac{1}{\kappa} \frac{\partial c_m(x,t)}{\partial x}. \quad (13)$$

The non-dimensional length of the domain is  $L = UL_x/D$  and the dimensionless length of the L and AL zones is  $L_p = UL_{plate}/D$ . The non-dimensional initial concentration is

$$c_m(x,0) = \begin{cases} 1/\alpha, & \text{for } x \in [x_{in}, x_{in} + l], \\ 0, & \text{elsewhere,} \end{cases} \quad (14)$$

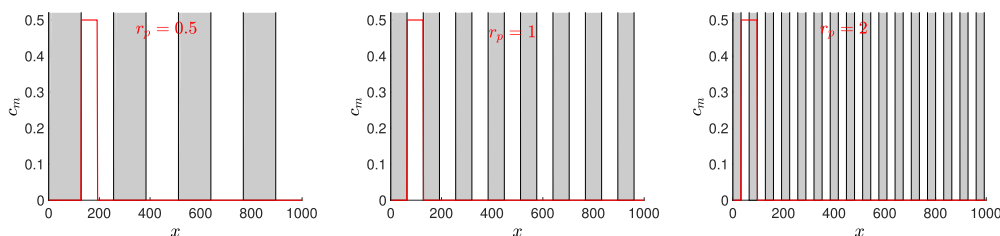
where  $l = UW/D_x$  is the non-dimensional width of the injected sample and  $x_{in}$  is the initial position of the rear interface of the sample.

#### 2.4. Parameter values and numerical method

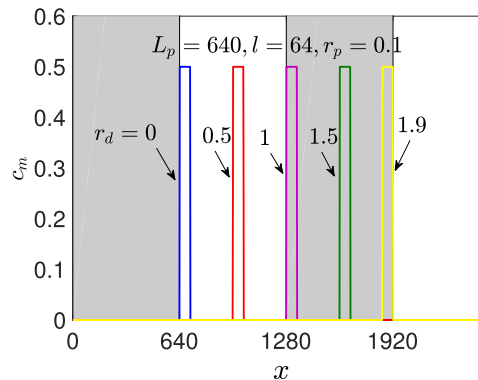
The solute mass balance Eq. (13) is a partial differential equation with variable coefficients that we solve using a Pseudospectral Fourier method (Canuto et al., 1988). Numerical stability is achieved using  $dx = 1$ ,  $dt = 0.02$ , for which the solute mass conservation is also verified. The solutions are observed to remain invariant with further decrease in grid size. The non-dimensional parameters of the problem are  $\alpha$ ,  $l$ ,  $\delta$ ,  $k$  and  $L_p$  that set the initial concentration  $c_m(x,0)$ , the rate of adsorption and describe the flow dynamics i.e. the propagation pattern of the solute and its rate of spreading. In addition to this, the initial position  $x_{in}$  of the slice also plays a crucial role in determining the spreading dynamics of the adsorbed solute (as explained in detail in Section 3.3).

Since there are a number of variables involved in our model, we combine some variables for which the influence on the propagation dynamics of the solute is observed to be dependent on each other. The values of parameters chosen in the simulations are:

- $\alpha = 2$ , which sets the initial mobile phase concentration  $c_m(x,0) = 0.5$ .
- The ratio of the width  $l$  of the solute slice to the width  $L_p$  of the zones is  $r_p = l/L_p$  (see Fig. 2). If  $r_p \leq 1$ , we study cases for which the sample width  $l$  is smaller than or equal to the alternation zone width  $L_p$  while if  $r_p > 1$  then  $l > L_p$ .
- The influence of the retention parameter  $k$  is studied for  $k = 1$  and 5.
- For a given value of  $x_{in}$ , the initial condition is observed to repeat itself after  $2 * L_p$ . The sample is thus assumed to be placed such that its rear starts within the second or third alternation zone i.e.  $x_{in}$  is varied as  $L_p + r_d * L_p$  with  $r_d \in [0,2)$  (see Fig. 3).
- Simulations run up to  $t = 50000$  and we fix  $l = 64$ ,  $L = 32768$ . So ratio of the sample length to the column length is  $\frac{l}{L} = 0.002$ , which is typical of experimental conditions in chromatographic columns.



**Fig. 2.** Influence of the parameter  $r_p = l/L_p$  on the geometry of the L-AL alternance encountered by the mobile phase concentration profile  $c_m$ . The white zones correspond to L zones while the grey zones feature AL properties. For a fixed value of  $l$ , taken here equal to 64, an increase in  $r_p$  corresponds to a decrease of the zone width  $L_p$ . If  $r_p < 1$ , the initial sample can be contained within one either pure L or pure AL zone depending on the value of the initial position of the sample given by  $r_d$ . Here  $r_d = 0$  and the sample starts in a L zone. If  $r_p > 1$ , the sample initially covers more than one zone.



**Fig. 3.** Influence of the parameter  $r_d$  on the initial position of the sample for  $r_p = 0.1$  here. For  $0 < r_d \leq 1$ , the rear part of the sample starts in a L zone while for  $1 < r_d \leq 2$ , the rear part starts in an AL zone.

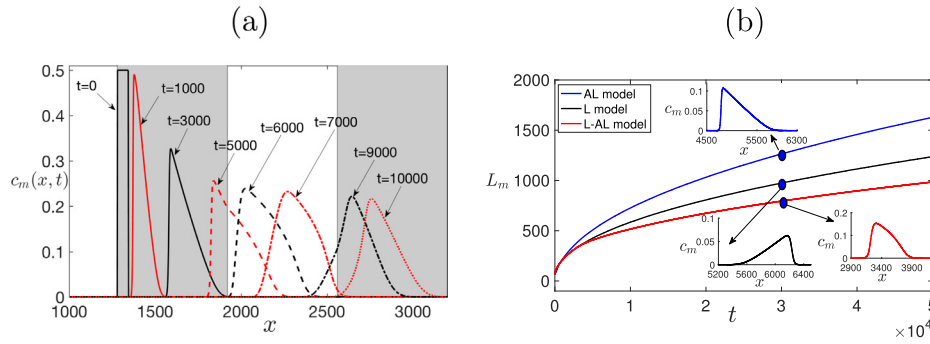
In the next section, we analyze the influence of varying the parameter values on the propagation and spreading dynamics of the solute.

### 3. Results

The parameters on which the flow dynamics of the solute depends are here reduced to  $\delta$  (the ratio  $b_L/b_{AL}$  of the nonlinear adsorption parameters), the retention parameter  $k$  controlling the strength of the adsorption, the geometrical parameter  $r_p$  comparing the relative width of the sample to that of the alternation zones and  $r_d$ , the parameter controlling whether the initial position of the rear part of the injected sample is in a L or AL zone. Before analyzing the effect of varying the values of these parameters, let us examine the qualitative influence of the alternance of L and AL zones on the dynamics.

#### 3.1. Accordion effect and reduction of peak widening

Fig. 4(a) shows a typical displacement of a finite width sample into a L-AL alternating geometry. We take here  $k = 5$  corresponding to a quite strong adsorption effect and  $\delta = 1$  for  $b_L = b_{AL} = 1$  i.e. the adsorption parameter is of the same strength in the L and AL zones. The width  $l$  of the sample is 1/10 of the length  $L_p$  of the L/AL zones such that the geometrical parameter  $r_p = l/L_p = 0.1$ . For  $r_d = 1$ , the left part of the sample starts at the initial time in an AL zone and, as  $r_p < 1$ , the sample is initially totally contained in the AL zone (see Fig. 4(a) at time  $t = 0$ ). Once the displacement starts, the rear part of the sample is sharpening while its frontal peak is widening because of the anti-Langmuir adsorption properties of the AL zone in which the sample starts its journey in the porous matrix (see Fig. 4(a) at times



**Fig. 4.** (a) Spatial concentration profiles of the mobile phase  $c_m(x, t)$  for  $k = 5$  in a L-AL alternate geometry for  $b_L = b_{AL} = 1$ ,  $r_d = 1$ ,  $r_p = 0.1$  at successive times. (b) Temporal evolution of the spreading length  $L_m$  of the adsorbed solute for  $k = 5$  in a L model ( $b_L = 1$ ), AL model ( $b_{AL} = 1$ ) and L-AL model ( $b_L = b_{AL} = 1$ ,  $r_p = 0.1$ ,  $r_d = 1$ ) with the corresponding peak profiles at the time shown by a bullet.

$t = 1000, 3000$ ). However, once the sample starts passing through a L zone, the reverse effect sharpens its front while diluting the rear part (see Fig. 4(a) at times  $t = 5000, 6000, 7000$ ). The alternation between sharpening and widening at both edges of the sample gives an accordion effect that, in the end, reduces the total broadening of the peak. This can be appreciated in Fig. 4(b) giving the temporal evolution of the spreading length  $L_m$ , computed as the length of the interval for which the solute concentration  $c_m \geq 0.001$  (De Wit et al., 2005).  $L_m$  is a measure of the widening of the peak. First, we note that the pure AL displacement gives a larger broadening of the sample than a pure L one because, for AL displacements, the rarefaction wave is formed in the direction of the flow, thus spreading due to rarefaction is further enhanced. The peak profiles for L and AL displacements at time  $t = 3 \times 10^4$  are shown in the inset of Fig. 4(b) (Rana et al., 2019). It is seen that the L-AL alternation gives a smaller mixing length at a given time than both pure L or AL systems, thanks to this accordion effect. Let us now see how this reduction of peak widening in the L-AL system depends on the various parameters of the problem.

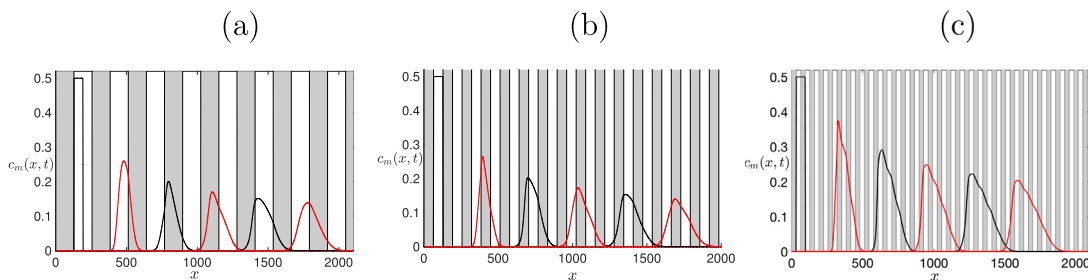
### 3.2. Influence of $r_p$

Fig. 5 shows the concentration profiles  $c_m(x, t)$  of the solute in the mobile phase for different values of  $r_p$  when the other parameter values are fixed. When the alternation zone width is larger than the initial sample width i.e.  $r_p \leq 1$ , the solute peak shape behaves in an Anti-Langmuir way in the AL zones and smoothly switches to a Langmuir behavior in the L zones (see Fig. 5(a) and (b)). On the contrary, when  $r_p > 1$ , the solute concentration distribution encounters rapid local expansions and contractions whenever the zone switch happens inducing undulated profiles (see Fig. 5(c)). The temporal evolution of the spreading length  $L_d$  given in Fig. 6 shows that the solute spreading for the L-AL models is always smaller for all  $r_p$  scanned than for transport in the single

site adsorption Langmuir or anti-Langmuir systems. This is because the peak tailing, which results in concentration overloading related band widening of the Langmuir or anti-Langmuir adsorbed solute, is prominently reduced with the alternance of L and AL zones. In addition, in the L-AL model,  $L_m$  varies with  $r_p$ . It is observed that  $L_m$  is smaller for  $0 < r_p \leq 1$  in comparison to  $r_p > 1$  cases. Thus least spreading in the L-AL system can be obtained when the width of the sample is smaller than the width of the alternation zones i.e.  $l < L_p$ . In the limiting case of  $r_p \rightarrow 0$ , or equivalently  $L_p \rightarrow \infty$  for a finite  $l$ , the solute profile depicts the features of a single site model of either Langmuir or anti-Langmuir properties depending upon the initial position of the sample. On the other hand, for  $r_p \rightarrow \infty$  or also  $L_p \rightarrow 0$ , we recover symmetric solute peaks as in the case of linear adsorption.

### 3.3. Influence of $r_d$

In the L-AL system, we find that the initial position of the sample i.e. whether it is initially injected into a L or an AL zone has an influence on the peak profile and on the spreading dynamics of the adsorbed solute. This can be appreciated in Fig. 7 giving the spatial concentration profiles of the solute in the mobile phase at successive times for different values of  $r_d$  for  $k = 5$ ,  $b_L = b_{AL} = 1$ ,  $r_p = 1$ . Depending on the initial position of the sample i.e. depending on  $r_d$ , a difference is observed in the amplitude and shape of the solute peak. During the propagation, the width of the flat top solute decreases and, following the interaction of the two interfaces, becomes a point. After that, the solute peak height starts decreasing from the initial concentration  $1/\alpha$  in the course of time. Therefore, if the initial position of the solute sample in a L-AL system is such that both interfaces undergo widening in the early times (for instance if the frontal part of the sample is in an AL zone while its rear is in a L zone), the peak height starts decreasing faster. On the contrary, if the initial position of the solute sample is such that



**Fig. 5.** Spatial concentration profiles in the mobile phase  $c_m(x, t)$  for  $k = 5$ ,  $\delta = 1$  with  $b_L = b_{AL} = 1$ ,  $r_d = 0$  and (a)  $r_p = 0.5$  (b)  $r_p = 1$  (c)  $r_p = 2$  at times  $t = 0, 2000, 4000, 6000, 8000, 10000$ .

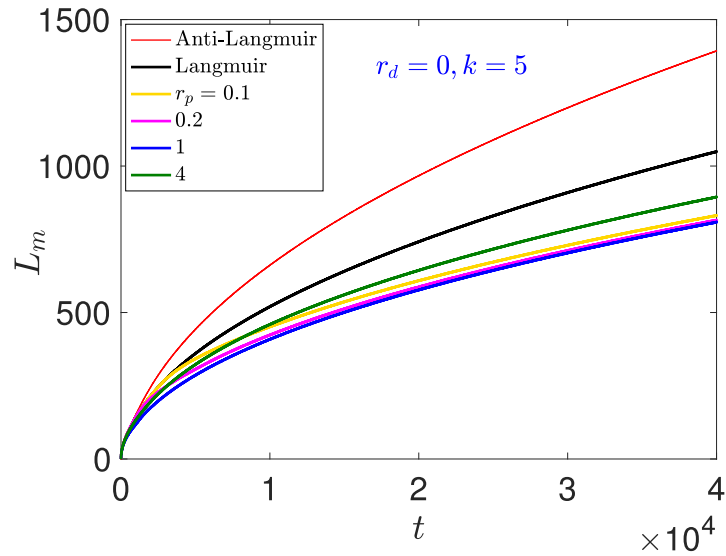


Fig. 6. Temporal evolution of the spreading length  $L_m$  of the adsorbed solute for different values of  $r_p$ , at fixed  $r_d = 0$ ,  $k = 5$ ,  $\delta = 1$ .

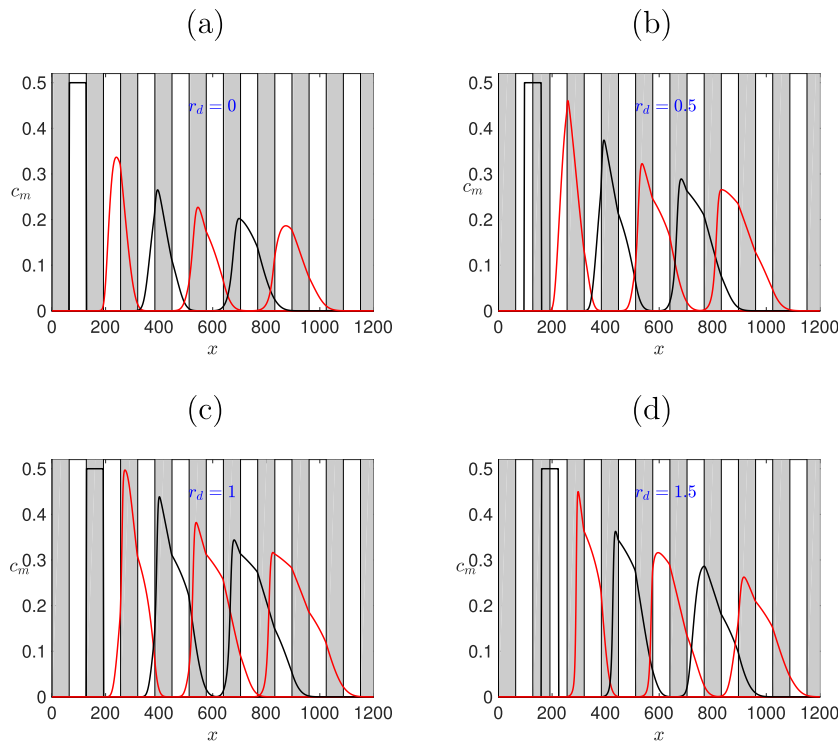
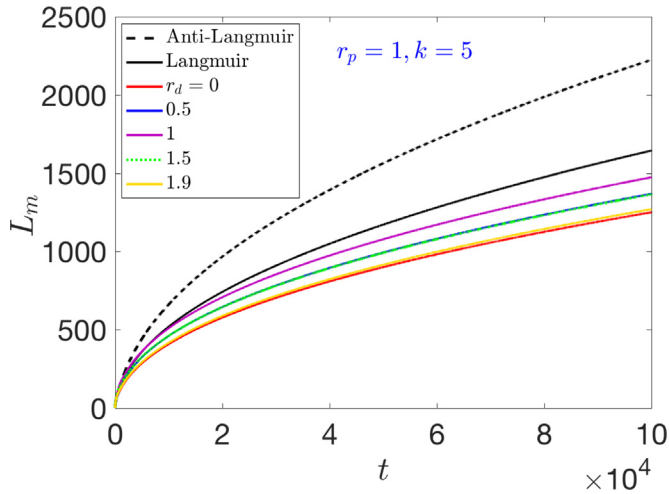


Fig. 7. Concentration profiles in the mobile phase  $c_m$  with  $r_p = 1$ ,  $\delta = 1$ ,  $k = 5$  for (a)  $r_d = 0$  (b)  $r_d = 0.5$  (c)  $r_d = 1$  (d)  $r_d = 1.5$  at times  $t = 0, 1000, 2000, 3000, 4000, 5000$ .

both interfaces undergo sharpening in the early times (for instance frontal part in L and rear part in AL), then the decrease of the peak height occurs later. For instance, in Fig. 7(a), with  $r_d = 0$ , the frontal and rear interfaces of the solute both undergo expansion when the displacement starts as they spend the early times in the AL zone and L zone, respectively. This results in their early interaction and a faster decrease of the amplitude of the solute peak with time. In Fig. 7(c), we see that with  $r_d = 1$ , the frontal and rear of the solute undergo initially sharpening as they spend early times in the L zone and AL zone, respectively. This results in their late interaction and a delayed decrease in the amplitude of the solute peak with time. The smallest amplitude is therefore observed for  $r_d = 0$  and the largest one for  $r_d = 1$ . Intermediate situations are obtained

for other values of  $r_d$  (see Fig. 7b and d). Since the initial position of the solute determines the early time interaction of the solute with the L-AL alternation, it has thus an effect on the amplitude of the solute.

The corresponding temporal evolution of the spreading length  $L_m$  given in Fig. 8 shows again that  $L_m$  is always smaller for the L-AL model than in the single site Langmuir or anti-Langmuir systems. In addition, in the L-AL model,  $L_m$  varies with  $r_d$ :  $L_m$  grows non-monotonically with  $r_d$  i.e., for  $0 \leq r_d \leq 1$ ,  $L_m$  increases with  $r_d$ , while it decreases for  $1 < r_d < 2$ . For  $r_p = 1$  the smallest width is obtained for  $r_d = 0$ . Thus the most efficient situation in terms of decreasing concentration overloading related band widening is thus to start in a L zone. This suggests that the solute dynamics



**Fig. 8.** Temporal evolution of the spreading length  $L_m$  for different initial position  $r_d$  of the sample for  $r_p = 1$ ,  $\delta = 1$  and  $k = 5$ .

carries its history along the displacement for a long time when passing through alternating L and AL zones.

**3.4. Influence of  $k$  on the solute spreading**

For a linear adsorption, it has been shown that the larger the value of the retention parameter  $k$ , the more the solute is retained on the porous matrix and thus the slower it propagates (Mishra et al., 2009). In the case of L-AL alternance, larger values of  $k$  imply that the sample will interact with each zone more strongly and will thus be more influenced by the multiple adsorption site situation in comparison to the small values of  $k$ .

This can be appreciated on Fig. 9(a) comparing the concentration profiles  $c_m(x, t)$  at different times for  $k = 1$  and 5 keeping  $r_p$ ,  $\delta$  and  $r_d$  fixed. We see that, for  $k = 5$ , the stronger retention on the porous matrix induces a slower transport of the sample, a stronger influence of the L-AL alternation and a smaller broadening than with  $k = 1$ . The longer interaction time of the solute with the corresponding zones when  $k$  is larger favors thus a more efficient accordion effect leading to better resolved peaks. This is confirmed by analyzing the spreading length of the adsorbed solute for different  $L_m$  for these two values of  $k$  as plotted in Fig. 9(b).  $L_m$  is always smaller for the L-AL model than for the pure L or AL cases,

irrespective of the value of  $k$  and the smallest widening for the L-AL system is obtained for larger  $k$ .

**3.5. Influence of  $\delta$  on the solute spreading**

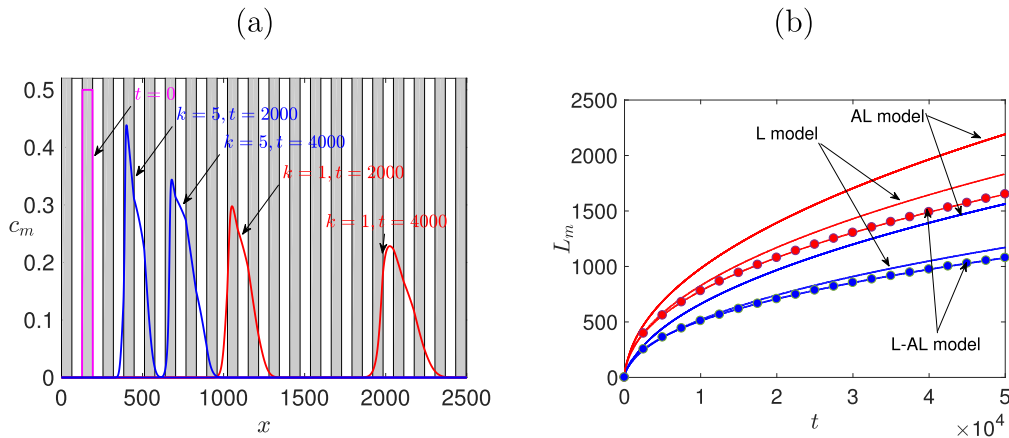
The non-dimensional parameter  $\delta = b_L/b_{AL}$  compares the strength of the non-linear adsorption on Langmuir zones to the one on anti-Langmuir zones. If  $\delta = 1$ , we have  $b_L = b_{AL}$ , which implies that the magnitude of the deviation from a linear adsorption behavior is identical for both studied cases (with however opposite signs, resulting in Langmuir and Anti-Langmuir behavior, respectively). If  $\delta$  is increased above one, the influence of L zones is more and more pronounced with regard to that of the AL zones and, vice versa, for  $\delta < 1$ , AL zones dominate the solute transport dynamics. To illustrate this, Fig. 10 compares the concentration profiles of the solute for  $\delta = 0.5, 1, 2$ . We see that, for  $\delta = 0.5$ , the rear of the sample tends to a shock wave while the frontal part has more tailing, which shows the dominance of the AL zones. On the contrary, for  $\delta = 2$ , the L zones can counteract this and “re-dress” the profile to reach a more symmetric peak shape.

Thus, for the applications where reducing the concentration overloading related band widening of the solute is essential to increase the efficiency of the method, an alternation of L and AL zones provides a robust mechanism to reduce the spreading of the solute. It remains to assess more quantitatively which combinations of the four parameters gives the best reduction of peak broadening. This is analyzed in the next section where a strategy to reduce the peak broadening is proposed.

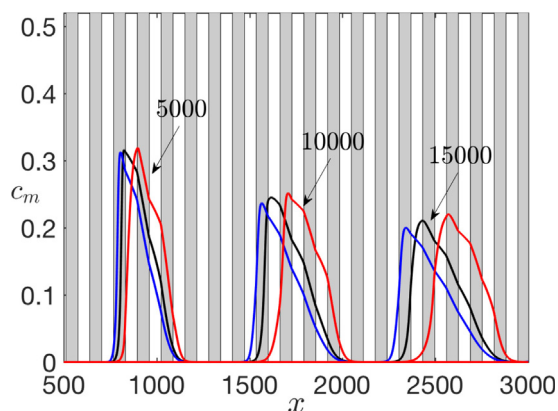
**4. Quantitative analysis**

From the above results, it is clear that the global features of the solute displacement in a L-AL system, like the widening of the solute peaks, are largely controlled by the adsorption parameters ( $k, \delta$ ) but also by the parameters  $r_p$  and  $r_d$  related to the geometry of the alternation between the L and AL zones.

Figs. 11 and 12 show phase diagrams giving the amplitude of the spreading length  $L_m$  at the final time of the simulation in the parameter space ( $r_p, r_d$ ) for  $k = 1$  or 5 and 3 different values of  $\delta$ . The colors on the graph vary from red for the ( $r_p, r_d$ ) couple of parameters at which  $L_m$  is maximum to blue for the minimal  $L_m$  values. The absolute values of  $L_m$  for a given color is given in the color bar to the right of each panel but in all cases red and blue correspond to the maximum and minimum values.



**Fig. 9.** (a) Concentration profiles in the mobile phase  $c_m$  at different times for  $k = 1$  (red) and  $k = 5$  (blue) with  $r_d = 1$ ,  $r_p = 1$ ,  $\delta = 1$ . (b) Temporal evolution of the corresponding spreading length  $L_m$  and comparison with the pure L and AL cases.



**Fig. 10.** Concentration profiles in the mobile phase  $c_m$  for  $k = 5$  at different times for  $\delta = 0.5$  (blue), 1 (black) and 2 (red) with  $r_d = 1$ ,  $r_p = 1$ . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

#### 4.1. Quantitative analysis of spreading lengths values

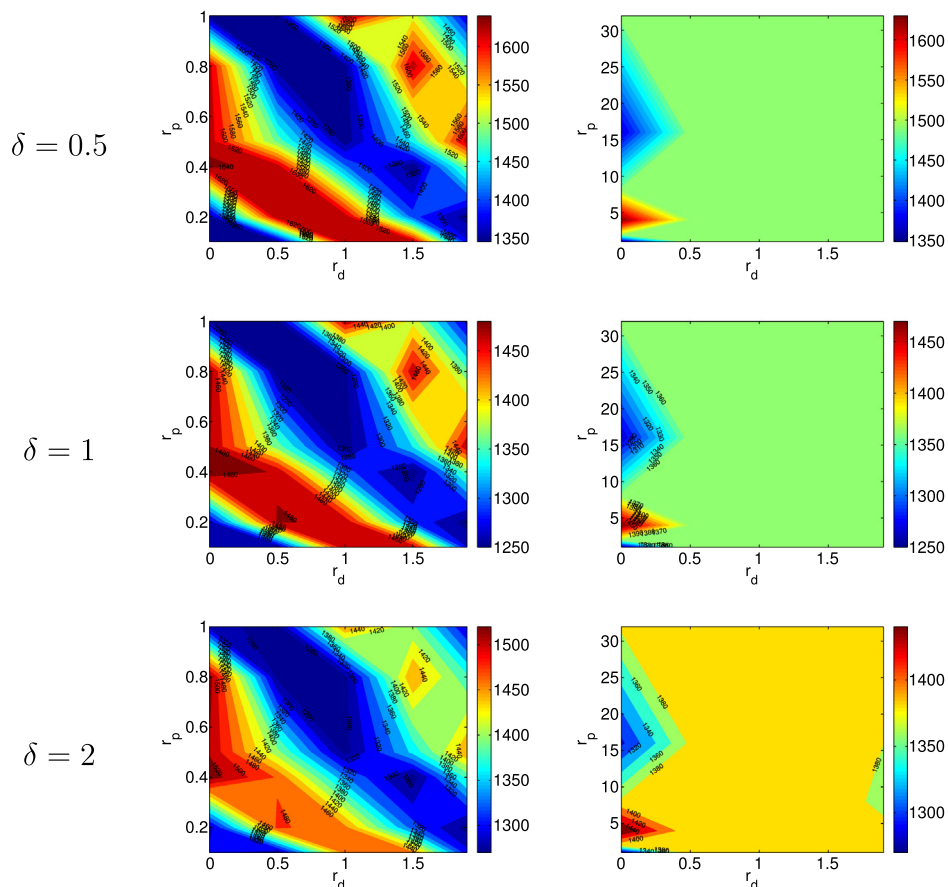
Figs. 11 and 12 show the phase diagrams of  $L_m$  for  $k = 5$  and  $k = 1$  respectively for three different values of  $\delta$ . To be able to compare the situation with a single site model, we fix  $b_{AL} = 1$  and vary  $b_L$  to get different values of  $\delta = b_L/b_{AL}$ . Specifically, we take  $b_L = 0.5, 1$  and  $2$  to get the values  $\delta = 0.5, 1, 2$  respectively.

The phase diagrams show a large variation of the final values of  $L_m$  when  $r_p \leq 1$  (left column) for all values of  $r_d$  and  $\delta$ . On the contrary, for  $r_p > 1$  (right column), the spreading length remains

in a particular color zone for  $r_d > 0.5$ . This shows that the influence of  $r_d$  is more pronounced on the solute spreading when the alternation zone width  $L_p$  is larger than the sample width  $l$ . Nevertheless, in all heterogeneous cases, the widening of the peak is smaller than the one in a pure homogeneous L or AL system. To appreciate this, we compare in Table 1 the spreading length  $L_L$  or  $L_{AL}$  at the final time  $t_{fin}$  for a single L or AL site model respectively, with the least spreading  $L_{min}$  and maximum spreading  $L_{max}$  obtained at the same time in the L-AL model. We see that, in the L-AL cases, the width of the solute peaks is always smaller than that of the pure L or AL cases. The gain in peak width reduction varies however with the specific combination of the parameter values. To quantify the gain in peak width reduction we compute the percentage of maximum gain compared to a pure AL column as  $G_{AL} = \frac{L_{AL} - L_{min}}{L_{AL}} \times 100$ . A gain of decrease in peak width as high as 43.82% for L-AL displacement in comparison to a single AL site model is achieved. A similar measure gives the gain with respect to a pure L column as  $G_L = \frac{L_L - L_{min}}{L_L} \times 100$ . A maximum gain of 32.20% in decrease in peak width for L-AL displacement is achieved in comparison to a single L site model.

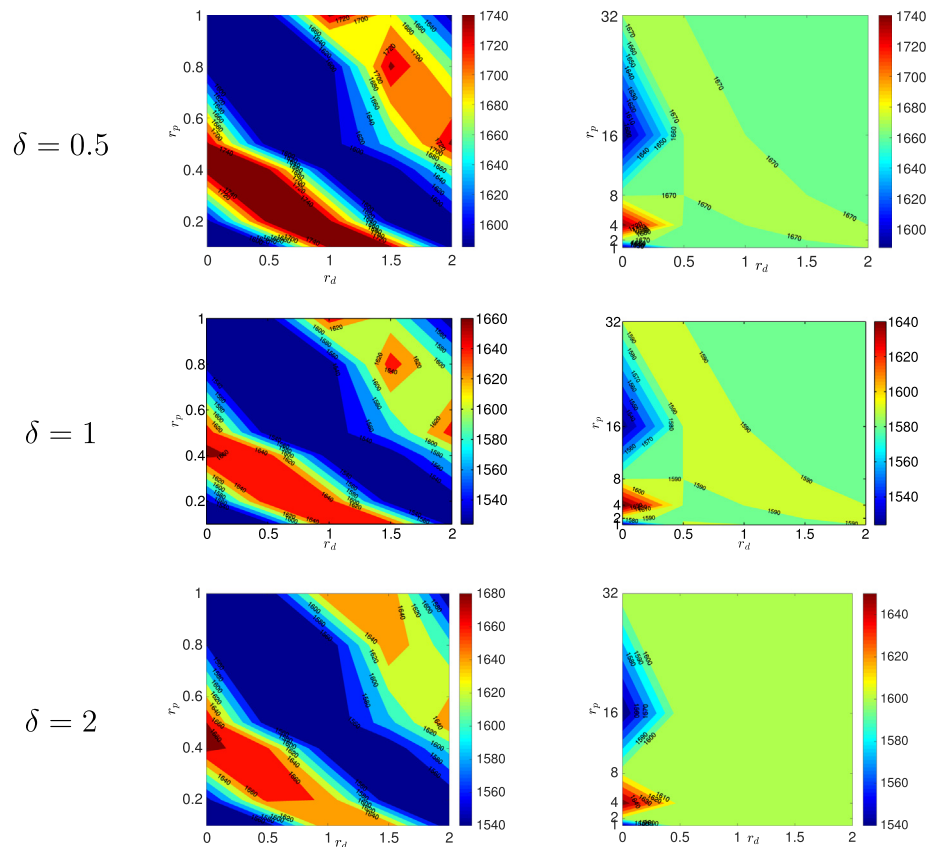
#### 4.2. Strategy to reduce the peak broadening

The above results allow to design optimal L-AL heterogeneity configurations of chromatographic column or optimal configurations for practical engineering applications to reduce the mixing length of the solute. Although the L-AL model always results in a smaller solute spreading than the classical single site model, an improved performance can be obtained by a suitable choice of



**Fig. 11.** Phase diagrams giving the values of  $L_m$  at  $t = 10^5$  in the  $(r_p, r_d)$  phase space for  $k = 5$  and different values of  $\delta$ . The left column refers to the case  $r_p \leq 1$  while, in the right one, we have  $r_p > 1$ .





**Fig. 12.** Phase diagrams giving the values of  $L_m$  at  $t = 50000$  in the  $(r_p, r_d)$  phase space for  $k = 1$  and different values of  $\delta$ . The left column refers to the case  $r_p \leq 1$  while, in the right one, we have  $r_p > 1$ .

**Table 1**

Table of  $L_m$  at  $t_{fin}$  for different values of  $k, \delta$  at fixed  $b_{AL} = 1$  and variable  $b_L$  in the case of a pure Langmuir ( $L_L$ ) or Anti-Langmuir ( $L_{AL}$ ) systems.  $L_{min}$  and  $L_{max}$  give the minimum and maximum values of  $L_m$  for an L-AL system when  $(r_p, r_d)$  are varied (see Figs. 11 and 12).

| $k$ | $\delta$ | $t_{fin}$       | $L_L$ | $L_{AL}$ | $L_{min}$ | $L_{max}$ | $G_{AL}$ | $G_L$ |
|-----|----------|-----------------|-------|----------|-----------|-----------|----------|-------|
| 5   | 0.5      | $10^5$          | 1463  | 2225     | 1347      | 1646      | 39.46    | 7.93  |
| 5   | 1        | $10^5$          | 1645  | 2225     | 1250      | 1500      | 43.82    | 24.01 |
| 5   | 2        | $10^5$          | 1876  | 2225     | 1272      | 1530      | 42.83    | 32.20 |
| 1   | 0.5      | $5 \times 10^4$ | 1663  | 2192     | 1586      | 1754      | 27.65    | 4.63  |
| 1   | 1        | $5 \times 10^4$ | 1830  | 2192     | 1524      | 1665      | 30.47    | 16.72 |
| 1   | 2        | $5 \times 10^4$ | 2096  | 2192     | 1540      | 1688      | 29.74    | 26.53 |

optimal alternation zone width to sample width ratio, optimal choice of initial zone in which to start the injection and relative strengths of the L/AL zones. As stated previously, different combinations of  $r_p$  and  $r_d$  affect dramatically the performance of the L-AL model. We have explored a large number of different configurations looking for a maximum output efficiency. We find that the combinations of  $r_d$  and  $r_p$  giving the maximal reduction in concentration overloading related band widening are the following:

- For  $r_d \in [0, 0.5], r_p \in (0, 0.2] \cup [0.8, 1] \cup (8, 32)$ .
- For  $r_d \in [0.5, 1.5], r_p \in [0.4, 0.8]$ .
- For  $r_d \in [1.5, 2], r_p \in (0, 0.4]$ .

The larger the values of  $k$ , the larger the effect of this reduction in sample spreading.

## 5. Conclusion

We have analyzed theoretically the transport properties of a sample of solute injected in a heterogeneous porous matrix alter-

nating in space regions featuring Langmuir (L) and Anti-Langmuir (AL) adsorption isotherms. This alternation induces an accordion effect reducing the concentration overloading related band widening of the peak. We have developed a theoretical model describing displacement in this L-AL system in which the important parameters of the problem are the adsorption parameter  $\delta = b_L/b_{AL}$  comparing the intensity of the nonlinear adsorption isotherm parameters, the retention parameter  $k$  controlling the strength of the adsorption, the geometrical parameter  $r_p = l/L_p$  comparing the relative width  $l$  of the sample to the length  $L_p$  of the L/AL zones and  $r_d$ , the parameter controlling whether the position of the rear part of the injected sample is in a L or AL zone at  $t = 0$ .

We find that, whatever the values of the parameters scanned here, the L-AL alternation always give a smaller peak broadening than the pure L or AL cases. The widening reduction increases when the adsorption intensity  $k$  increases. The geometry of the L-AL alternation is found to have an important influence. If the width of the L/AL zones is very small (i.e.  $r_p$  tends to infinity), the accordion effect cannot be effective and the system recovers symmetric profiles typical of linear adsorption. On the contrary, pure L

or AL systems are recovered for very large zones ( $r_p \rightarrow 0$ ) depending whether the sample is injected into a L or AL zone. For intermediate values of  $r_p$ , broadening reduction is obtained, the efficiency of which further depends on the zone in which the sample is injected initially, which is controlled by the parameter  $r_d$ . If the sample width and value of  $r_d$  are such that the frontal part of the sample experiences at the beginning of the displacement a sharpening in a L zone while its rear also sharpens because it crosses at early times an AL zone, then the widening effect is delayed and the peak broadening will be the smallest. A further control of the relative weight of the L or AL behavior can be obtained by tuning the parameter  $\delta$ . We have performed a characterization of the influence of varying these various parameters on the dynamics and have given their optimal combination of values to reduce the concentration overloading related band widening. Our results pave the way to developing new heterogeneous porous matrices alternating zones of different adsorption properties to optimize the reduction of concentration overloading related band widening. The concept is quite general. We have demonstrated it here with an alternation of two zones with Langmuir and Anti-Langmuir adsorption properties of equal width but the analysis can be straightforwardly adapted to more complex geometries with zones of different lengths and with different adsorption isotherms. Allowing for more than two different adsorption regimes will further increase the possible selectivity of the control strategy. Experimental demonstration of the efficiency of our theoretical concepts could for instance be obtained using micro-pillar array chips (Futagami et al., 2017; Callewaert et al., 2014).

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