

Two-Dimensional Continuous Model in Bimolecular Reactive Transport

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Abstract

In this work, a continuum 2D model is proposed to study the interaction at the interface of reactive transport processes in porous media. The analysis of the segregation produced by poor reactant homogenization at the poral scale is addressed by a parametric heuristic model that considers the relative gradient of the reacting species involved in the process. The micro inhomogeneities are incorporated by means of longitudinal and transversal mechanical dispersion coefficients. A two-dimensional continuous model for the bimolecular reactive transport is considered where modelling parameters are estimated numerically from experimental data. A competitive effect between segregation and dispersion is observed that is analyzed by means of numerical experiments. The two-dimensional model reproduces properly both the total mass of the product as well as its increase with the velocity of flow and the inhomogeneity of the advanced front. The methodology used is simple and fast, and the numerical results presented here indicate its effectiveness.

Keywords

Bidimensional Model, Transverse Dispersion, Segregation, Parameter Estimation

1. Introduction

The number of studies related to the transport of reactive species of dissolved compounds in porous media has considerably increased during the last few years. Generally, the spatial-temporal distribution of the solutes is significantly influenced by the variations at the microscale of the variables that control the reactive transport process (concentration, velocity) caused by the absence of homogeni-

zation, which cannot be addressed by a continuous model. Hence, when flow processes in a porous media with multiple reactive species are studied, it is important to consider the nature of reactions and the role of small-scale fluctuations (Edery *et al.*, 2013) [1].

There exists a negative correlation between the product of the concentration fluctuations around the average value of reactants (Kapoor *et al.*, 1997) [2] that describes the influence of flow spatial variation at the microscale on the average concentrations of solutes and on the reaction rate. An effective reaction rate can be modelled by incorporating a segregation term that depends on the product of the gradients of the solute concentrations (see also Kapoor *et al.*, 1998) [3].

Then, the processes of dispersion and mixing are not straightforward and deserve a deeper analysis. Cirpka (2002) [4] considers that the heterogeneity of the velocity field influences the coefficient of dispersion. So, the dispersion coefficient obtained in non-reactive transport cannot be used to model the reactive transport under the same flow conditions. Oates and Harvey (2007) [5] present a model of reactive transport that describes the segregation and mixing of reactants at the small scale by their joint distribution. Meanwhile, Willingham *et al.* (2008) [6] evaluate the effects of the porous media geometry in transversal mixing.

In Gramling *et al.*'s (2002) study [7], the authors present experimental results corresponding to an irreversible bimolecular reaction $A + B \rightarrow C$ and analyse the process by means of a model that assumes that solutes are instantaneously mixed, the Standard Pore-Scale Mixed (SPSM) Model. This continuum approach produces erroneous results since reactants are considered homogenized in the Darcy scale, but they are not perfectly mixed at the poral scale where chemical reactions occur (see also Raje & Kapoor, 2000) [8].

The quantitative treatment of fluctuations at the poral scale was approached in different ways. For instance, Edery *et al.* (2009, 2016) [9] [10] provide an interpretation of Gramling's experiment via a continuous time random walk particle tracking approach. Alhashmi *et al.* (2015) [11] develop a particle tracking model for flow and transport while the reaction occurs with a randomly assigned probability. Sanchez-Vila *et al.* (2010) [12] reinterpret the same experiment and describe the macroscopic chemical behaviour of the system by means of a kinetic reaction rate. Differences in the velocity of species at the poral scale are considered by means of an effective dispersion coefficient (to be adjusted). The segregation concept has also been analysed with a heuristic proposal by Rubio *et al.* (2008) [13], with a correction term that involves a phenomenological parameter that can be evaluated. In Ginn's (2018) [14] study, segregation zones generated by dispersion that limit mixing are considered. Besides, Gurung and Ginn develop a time-local model suitable for mixed boundary initial value transport problems by making the dispersion coefficient a function of the exposure time to the flow field (Gurung & Ginn, 2020) [15].

A very interesting review on the mixing-limited reaction of two solutes forming a product in porous media analysing experiments, theory, and numerical

methods was given by Valocchi *et al.* (2019) [16].

While most of the precedent treatments are based on a one-dimensional process, there are very few pieces of new research, but in a numerically simulated 3D porous media using a high-performance computing infrastructure. A set of high-resolution simulations were performed, and the results provided, which go beyond the original experiment, shed light on explaining the observations of Gramling's experiment (Sole-Mari *et al.*, 2023) [17].

On another way, Porta *et al.* (2012) [18] proposed a macroscopic mathematical model, considering an instantaneous reaction, going from the poral scale to the laboratory scale through an average in volumes. Chiogna and Bellin (2013) [19] propose to model the effect of incomplete mixing at scales smaller than the Darcy scale assuming that the mixing is distributed within a Representative Elementary Volume (REV) according to a Beta distribution.

In this paper, we use a model that changes the rate of reaction in the transport equation incorporating poral scale effects, or segregation. We model the problem considering a two-dimensional Advection Reaction Diffusion Equation (ADRE) model that includes three free parameters, one related to segregation term (α) and the other two for the dispersion (longitudinal D_x and transversal D_y). Our analysis is based on the experimental results of Gramling *et al.* (2002) [7].

The mathematical modelling of the segregation intensity (s) from first principles is not straightforward, so heuristic proposals (Kapoor *et al.*, 1997 [2]; Meeder & Nieuwstadt, 2000 [20]; Meile & Tuncay, 2006 [21]) are used to reproduce experimental results. An effective reaction term is defined as $\Gamma_{\text{eff}} = \Gamma(1 + s)$, where $s = c'_1 c'_2 / c_1 c_2$ is the segregation and c'_i is the variation of the concentration of the species " i " with respect to the average. Meyle and Tuncay (2006) [21] approach the product of the variation in concentrations of the species in terms of the product of the gradients of the macroscopic concentrations. Specifically, for reactive diffusive transport, we propose $s \approx (\alpha/\theta) \nabla c_1 \nabla c_2 / c_1 c_2$ where the parameter α depends on pore geometry, dispersivity and flux velocity, among other factors.

This article is organized as follows. In Section 2, the problem formulation is presented. In Section 3, the mathematical 2D model is stated. In Section 4, the numerical experiments are included and the results are discussed. Finally, the conclusions are given in section 5.

2. Problem Formulation

In a previous work (Cuch *et al.*, 2015) [22], we considered a 1D parameter estimation problem where the fitting parameters were the segregation and the dispersion coefficients, s and D , respectively. For the latter one, we obtained a lower value ($D = 0.0012 \text{ cm}^2/\text{s}$) than the one measured experimentally in batch ($D = 0.00175 \text{ cm}^2/\text{s}$), reported by Gramling *et al.* (2002) [7]. For the ADRE model, it is assumed that the transport process obeys the Fick's Law ($j = -D\nabla c$). Since the reaction time is several orders of magnitude smaller than the one of the advection and dispersion, and the production rate is high, reactive substances are quickly

consumed in the region of the reaction front. This generates a reaction product that also participates in the transport process separating the reactants and resulting in very large concentration gradients in that area. This fact might explain the differences between the estimated and the experimental D values.

In this work, we use a 2D model that considers poral scale issues using a macroscopic approach. We assume that variations in flow velocity are due to multiple microscopic causes like variation in velocity at pore scale and tortuosity of the path, as shown in **Figure 1**.

Dispersions in longitudinal (D_x) and transversal (D_y) directions to the flow are included in the model to consider deviations around the mean velocity. Since the two fluid regions mix not only in the flow (longitudinal) direction, but also in the transversal direction to the flow, both dispersion coefficients affect the mixing and, therefore, the reaction rate (Willingham *et al.*, 2008 [6]). We expect to obtain a smaller value for the longitudinal dispersion coefficient than the one for the 1D model, since the transversal dispersion coefficient will also contribute to the mixing.

3. Mathematical Model

We consider two reactive solutes A and B, with concentrations c_A and c_B respectively, where A displaces B with a macroscopic averaged velocity V , producing C at the interface, with a concentration c_C . Assuming a stationary adsorption process between the solid and liquid phases and homogeneity of the reactants, we have a reactive bimolecular transport process. For the bimolecular reactive transport problem studied by Gramling *et al.* (2002), we use a 2D model that considers the variations in the flow velocity. At each node of the two-dimensional computational domain, the velocity has the same direction as the corresponding to the macroscopic flow (X in **Figure 1**) and its average intensity, for a fixed X , is equal to that reported by Gramling *et al.* (2002) [7] (for example 0.0121 cm/s).

The process can be described by the following second order partial differential equation system:

$$\frac{\partial c_i(t, x, y)}{\partial t} + V_x(t, x, y) \frac{\partial c_i(t, x, y)}{\partial x} - D_x \frac{\partial^2 c_i(t, x, y)}{\partial x^2} - D_y \frac{\partial^2 c_i(t, x, y)}{\partial y^2} = R(t, x, y) \quad i = 1, 2, 3 \quad (1)$$

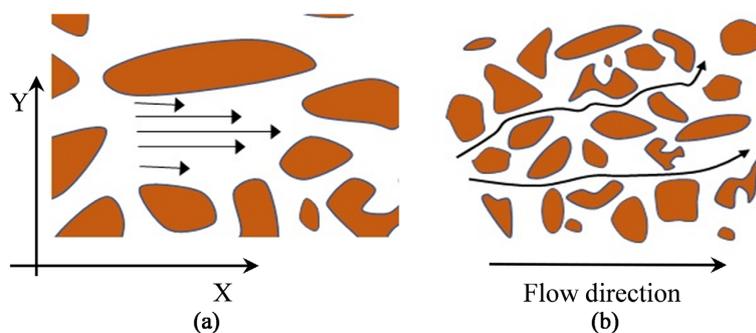


Figure 1. Velocity variation at poral scale. (a) Higher velocity towards the centre of the pores than near the surface of the solid matrix. (b) Tortuosity of the path.

where $(t, x, y) \in \Omega = [0, T] \times [0, L_x] \times [0, L_y]$ and $c_1 = c_A$, $c_2 = c_B$, $c_3 = c_C$

Here, $c_i(t, x, y)$ and $V_x(t, x, y)$ are the mean values for the corresponding Representative Elementary Volume (REV). The source term is modelled as an effective reaction term $R = \Gamma(1 + s)c_1c_2$, where s is the segregation factor (Kapoor *et al.*, 1997) [2], Γ is the reaction rate, $V_x(t, x, y)$ is the longitudinal velocity at each point of the spatial domain, D_x is the longitudinal dispersion coefficient and D_y is the transverse dispersion coefficient.

For the segregation factor, we use the heuristic model proposed by Meile and Tuncay (2006) [21] for a Diffusion Reaction Equation (DRE):

$$s = \frac{\alpha}{\theta} \frac{\nabla c_1 \cdot \nabla c_2}{c_1 \cdot c_2} \quad (2)$$

where the parameter α depends on the geometry of the pores, the dispersion, and the flow velocity. A similar function was used by Cuch *et al.* (2009) [23] for the one-dimensional case. The intensity of segregation, given by the negative correlation between the concentrations of reactants, can be seen as the product of the reactive concentration gradient: when the concentration gradient is low, the fluctuations will be small and the segregation negligible; while high gradients yield large fluctuations, and therefore a large segregation effect.

It can be seen in Equations (1) and (2) that the concentration of each species c_i , $i = 1, 2$ depends not only on the position and time but also on the parameters α , D_x and D_y , so that it can be written as $c_i(t, x, y, \alpha, D_x, D_y)$.

We use a finite difference method for the estimation of segregation and dispersion parameters (longitudinal and transversal) but other methods give similar results (Hou *et al.*, 2015) [24]. The numerical scheme is centred in space and forward in time, which guarantees a precision of first order in time and second order in space. As the reactants move by advection and mechanical dispersion, we use a velocity distribution with a dispersion of 20% around the average given by Gramling *et al.* (2002). We have tested other values of dispersion of velocity obtaining similar results. At each temporal step, we use an Operator Splitting technique (Wheeler & Dawson, 1987) [25], solving first the advection-dispersion equation and then, for a much shorter time interval, we solve the equation where only the source term is included (Rubio *et al.*, 2008) [13]. Then, the three parameters α , D_x and D_y are estimated by minimizing the square errors. The numerical method used to adjust the pre-processed experimental data is described by Cuch *et al.* (2015) [22].

4. Results

In Gramling *et al.*'s (2002) study [7], the authors reported, for a given flow ($Q = 2.67$ ml/min), the concentration of product C_C at each point x of the column, at four different instants (619 s, 916 s, 1114 s and 1510 s). Data from those profiles are used to minimize the square errors between the simulated and the pre-processed experimental data. The values of the characteristic constants of the experiment: reaction rate (Γ), length and height of the tube (L_x , L_y), porosity (θ) and initial

concentrations C_0 for both C_A and C_B , are assumed to be known (Gramling *et al.*, 2002) [7].

Figure 2 shows the results considering a flow rate $Q = 2.67$ ml/min. red circles correspond to the experimental data and the solid blue line correspond to our numerically simulated ones. It can be seen a good agreement between numerical simulation and experimental measurements.

Table 1 shows the average values of the adjusted parameters and the ratio between longitudinal and transversal mechanical dispersion. The results show that D_y is of the same order of magnitude as D_x , which justifies its inclusion in the 2D model.

Here, we also obtain a lower value of D_x (0.000846 cm²/s) than the estimated one using the one-dimensional model. This was expected since we have included the transverse coefficient D_y in the model. It also happens using other techniques, as reported by Ginn (2018) [14]. **Table 2** shows that variations around the average are negligible, being able to use their average values as representative for that flow.

On the other hand, **Figure 3** shows the results for the total product mass (integral of the profiles in **Figure 2**) for different settings for the previous work

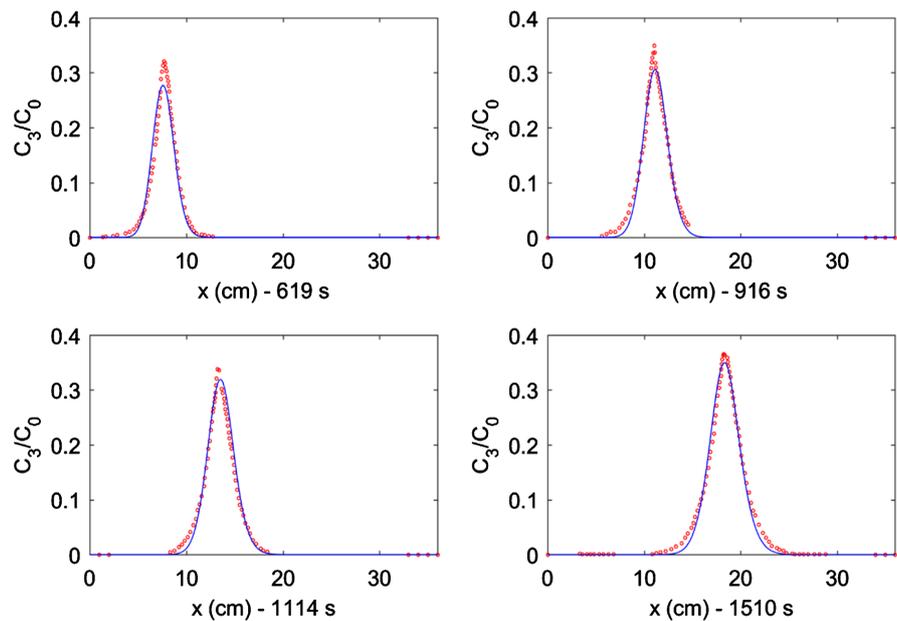


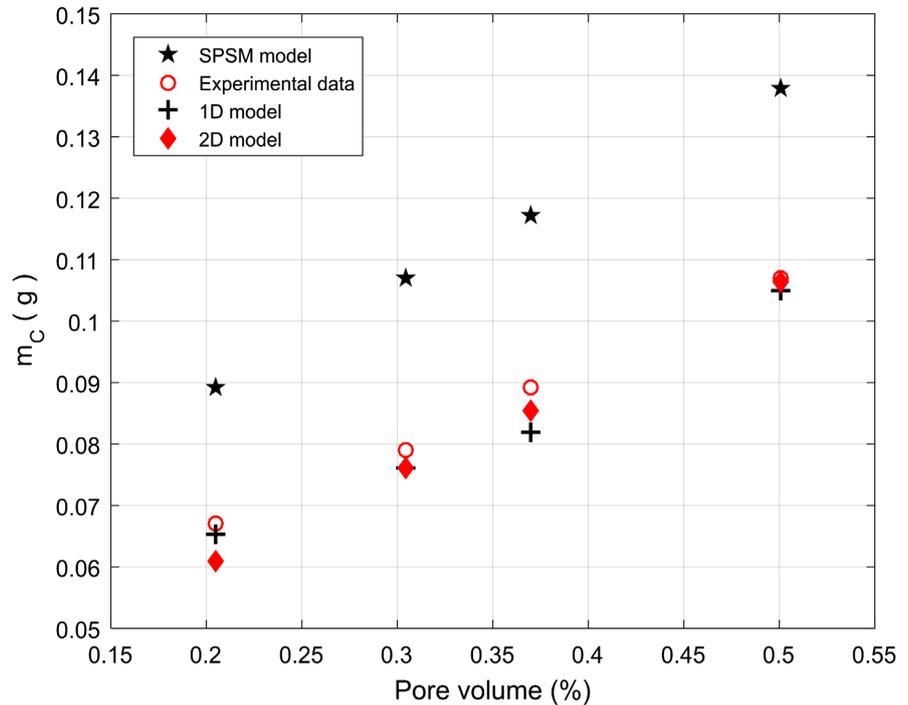
Figure 2. Circles correspond to the experimental data, solid line correspond to our simulation results for a flow rate of $Q = 2.67$ ml/min at times $T = 619$ s, 916 s, 1114 s and 1510 s. $C_0 = 0.02M$.

Table 1. Average values of the adjusted parameters $(\bar{\alpha}, \bar{D}_x, \bar{D}_y)$ and relation between longitudinal and transversal mechanical dispersion for a flow rate of $Q = 2.67$ ml/min.

$\bar{\alpha}$ (cm ²)	\bar{D}_x (cm ² /s)	\bar{D}_y (cm ² /s)	\bar{D}_x/\bar{D}_y
0.159	0.000846	0.000351	2.409

Table 2. Percentage variation of the adjusted parameters.

Q (ml/min)	T(s)	$\Delta\alpha$ (%)	ΔD_x (%)	ΔD_y (%)
2.67	619	-0.63	5.59	7.05
2.67	916	-0.63	-3.28	-1.78
2.67	1114	1.89	-1.63	-2.92
2.67	1510	-0.63	-0.68	-2.35

**Figure 3.** Total mass of product for several adjustments, one-dimensional and two-dimensional models.

(one-dimensional model) and the two-dimensional model, where an improvement of the 2D case can be observed.

The modelling of the ADRE by means of finite differences in 2D produces a better adjustment than the 1D model and shows an improvement in the results for longer time, suggesting that it takes some time to reach the proposed flow conditions. In fact, in the onset of the experiment there is a transitory regime, since initially only one of the solutes occupies the entire chamber, so that initially they are completely disaggregated. Then, the other solute is injected and mixing, and reaction start, and it takes time to reach stable values of speed and dispersion.

Gramling *et al.* (2002) [7] shows, in their Figure 5(b), for two other flow settings, the product concentration profile at just an instant: 157 s for a flow rate $Q = 16$ ml/min and at 20.23 s for $Q = 150$ ml/min. For those instants, the centre of the reaction front is approximately at $x = 13$ cm, which coincides with that of the advance front at 1114 s for the flow $Q = 2.67$ ml/min, being able, then, to com-

pare the production level of the product with respect to flow rate and dispersion around the maximum peak.

Table 3 shows the estimated segregation and longitudinal and transversal mechanical dispersion coefficients for the three flows given at approximately the same point of the device (equal pore volume). The mass of the product for each one of the three cases is also shown. It can be observed that as the flow increases, the longitudinal and transverse dispersion coefficients increase too. This is consistent with the theory that predicts that the dispersion is proportional to a power between 1 and 2 of the speed (Bear, 1988) [26]. Also, as the dispersion increases, the mixing increases too and with it increases the production of product.

In **Table 3**, it can also be observed the dependency of the mechanical dispersion coefficient on the velocity. The values obtained for D_x are lower than those reported in batch (Gramling *et al.*, 2002) [7]. Since the reaction time is several orders of magnitude smaller than the one for advection and dispersion, and the production rate is high, reactive substances are quickly consumed in the region of the reaction front generating a reaction product that also participates in the transport process.

By increasing the speed, the dispersion coefficient increases and with it the mixing and the product formation. **Figure 4** shows the widening of the reaction zone caused by the increase in dispersion. It should be noted that D_x increases with speed favouring the mixture. But when dealing with fast reactive processes, the reaction product is quickly generated around the central zone, which contributes to the separation of reactants (segregation) in a competitive process. In

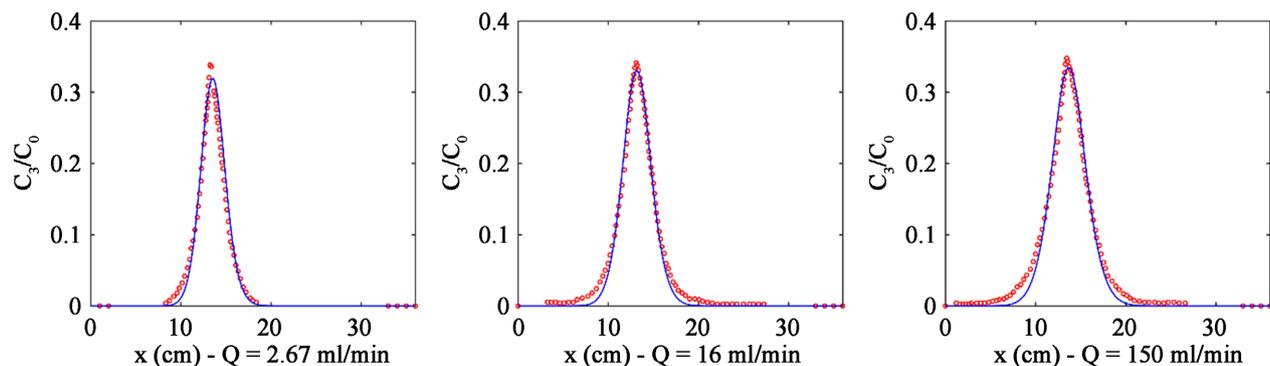


Figure 4. Best fit for different flows: $Q = 2.67$ ml/min, 16 ml/min and 50 ml/min. The advance front corresponds approximately to the same point of the device (equal pore volume). The circles correspond to the experimental data and the solid line to the simulated results.

Table 3. Estimated parameters values (α, D_x, D_y) different flow quantities (Q).

Q (ml/min)	v (cm/s)	T (s)	vT (cm)	α (cm ²)	D_x (cm ² /s)	D_y (cm ² /s)	M_c (g)
2.67	0.0121	1114	13.48	0.159	0.00084	0.00035	0.08543
16	0.0832	157	13.06	0.195	0.0085	0.005	0.10358
150	0.67	20.23	13.56	0.24	0.145	0.0964	0.12463

this sense, the magnitude of the reactant gradients depends on the values of the dispersion coefficient and the reaction rate.

We can compare the dependence of the segregation term on the velocity while the rest of the parameters are constant. The product formation rate, Γ , is the same for the three flow settings and the comparison occurs in approximately the same point in the chamber.

As the flow increases the product mass increases too (see **Table 3**), then the segregation term s must be lower (in absolute values), *i.e.* for the three cases of flow that we are considering.

$$|S_1| > |S_2| > |S_3| \quad (3)$$

$$\frac{|S_i|}{|S_{i+1}|} > 1 \quad (4)$$

On the other hand, based on the results of our numerical experiments,

$$\alpha_1 < \alpha_2 < \alpha_3 \quad (5)$$

$$\frac{\alpha_{i+1}}{\alpha_i} > 1 \quad (6)$$

From the Equation (2), considering the relations (4) and (6), we have,

$$\frac{|S_i|}{|S_{i+1}|} \cong \frac{\alpha_i}{\alpha_{i+1}} \frac{\left(\frac{|\nabla c_A \nabla c_B|}{c_A c_B} \right)_i}{\left(\frac{|\nabla c_A \nabla c_B|}{c_A c_B} \right)_{i+1}} \Rightarrow \frac{|S_i|}{|S_{i+1}|} \frac{\alpha_{i+1}}{\alpha_i} \cong \frac{\left(\frac{|\nabla c_A \nabla c_B|}{c_A c_B} \right)_i}{\left(\frac{|\nabla c_A \nabla c_B|}{c_A c_B} \right)_{i+1}} > 1 \quad (7)$$

That is to say,

$$\left(\frac{|\nabla c_A \nabla c_B|}{c_A c_B} \right)_i > \left(\frac{|\nabla c_A \nabla c_B|}{c_A c_B} \right)_{i+1} \quad (8)$$

According to expression (8), as the speed increases, the ratio of the product of the solute gradients with respect to the product of their average concentration decreases, given different effective reaction rates. Because of it, in cases like this, where the reaction rates coefficients are the same, we expect those reactive experiments (competitive process) that have higher segregation (less mass is produced for the same reaction rate) to show larger gradients with respect to concentration. So is the lesser dispersion that affects the mixing and therefore the production of the product of reaction.

Figure 5 shows our numerical result in the X - Y plane for the advancing front for $Q = 2.67$ ml/min at four times: 619 s, 916 s, 1213 s and 1510 s. We colour our results with the same colours used in **Figure 3(b)** by Gramling *et al.* (2002), for easy comparison (reproduced here in **Figure 6**). It is clearly observed that the concentration of reactants and product are not homogeneous in the reaction front. This inhomogeneity leads to an increase in cross-sectional dispersion and justifies the consideration of a two-dimensional model and the inclusion of D_y .

To analyse the predicting capacity of our model, we use the mean values of the

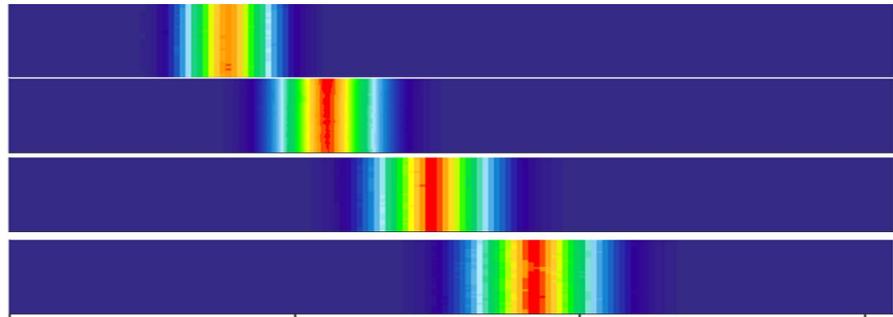


Figure 5. Our simulation for product concentration profile for 619 s, 916 s, 1114 s and 1510 s. Compare with **Figure 6** (Gramling *et al.*, 2002, Figure 3(b)).

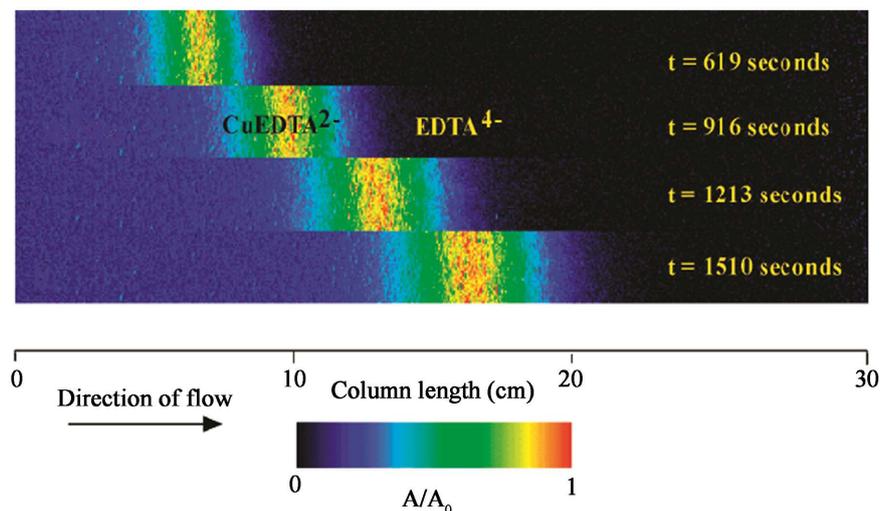


Figure 6. Product concentration profile for 619 s, 916 s, 1114 s and 1510 s (Gramling *et al.*, 2002 result, Figure 3(b), with permission).

three parameters obtained in the adjustment made (**Table 1**). We calculate the total product mass for different times, for flow rate of 2.67 ml/min, and we compare it with the experimental results, as shown in **Figure 7**. Gramling *et al.* (2002) [7] show the total product mass (the integral of the product concentration profiles throughout the cell) for several moments (results from Gramling *et al.* 2002, Figure 6(a), with permission).

We point out that our model does not consider the initial transitory regime due to the experimental setup. This fact explains the difference in the total mass for pore volume smaller than 0.15 %. This discrepancy is also observed in other models (Alhashmi *et al.*, 2015 [11]; Ginn, 2018 [14]). A good adjustment of our 2D model is observed once this initial transitory regime (when C_A begins to displace C_B) is overcome.

5. Conclusions

We present a continuous 2D model that incorporates a non-uniform velocity field and includes not only a longitudinal dispersion coefficient, but also a transversal mechanical dispersion coefficient, to analyse the segregation problem. This

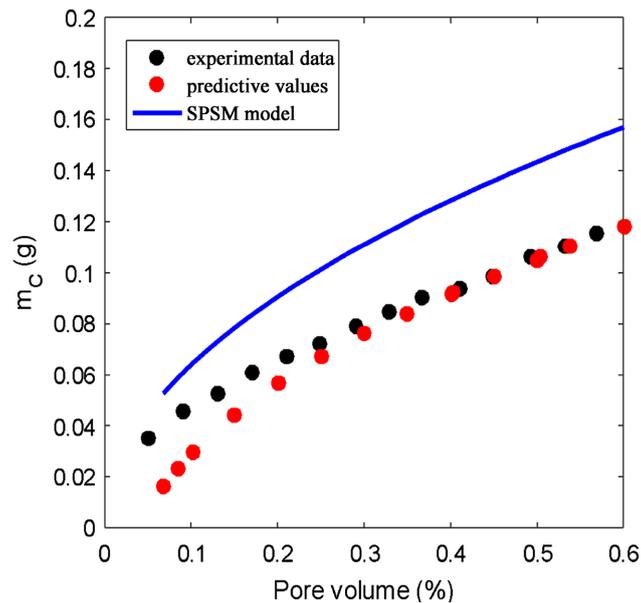


Figure 7. Total mass of product versus pore volume. In continue line, the SPSM prediction, in black circles the experimental results by Gramling *et al.* (2002, Figure 6(a), with permission) and in red circles our prediction, for a flow rate of 2.67 ml/min.

model was applied for the first time to a bimolecular reactive transport process and is part of a doctoral thesis

(<http://repositorio.ungs.edu.ar:8080/xmloi/bitstream/handle/UNGS/730/Cuch.pdf?sequence=1&isAllowed=y>).

The three modelling parameters (α , D_x and D_y) are estimated by minimizing the square errors when fitting the experimental results. A good agreement with the experimental data is obtained, as shown in **Figure 2**. The fact that D_y is of the order of D_x is worth noting and justifies the use of a 2D model since transversal dispersivity cannot be ignored.

The resulting estimated values for D_x are lower than those reported in the experimental setup that was measured in batch. It was observed the widening of the reaction zone was caused by the increase in the dispersion with the velocity. This should stimulate the mixture but, as the reaction time is very short, the reaction product is quickly generated around the central zone contributing to the segregation in a competitive process that makes it very difficult to carry out a detailed analysis of the process. By means of data fitting, we estimated the value of the parameter α that characterizes the segregation factors, and in this way, we have verified that as the velocity increases, the product of the solute gradients in relation to its average concentration decreases. In this sense, the magnitude of the gradients of the reactants depends on the values of the dispersion coefficient and the reaction rate.

Finally, we evaluate the predictive capacity of this model determining the total product mass. The resulting values are compared with the experimental values measured by Gramling *et al.* (2002), Figure 6(a), with permission. Good fitting was shown after 0.15% pore volume. In the experiment to pump the incoming

fluid through the porous plate, a syringe with five input ports was used. It is possible that the difficulty in modelling these initial moments is related to the time that takes the flow to distribute evenly in the porous medium across the width of the chamber, simulating a piston flow. This could also explain the advance of the fronts in the simulations with respect to the corresponding experimental ones. In our case, the numerical values obtained coincide with the experimental ones, obtaining a better approximation than the one previously obtained. We conclude that the two-dimensional model proposed here, reproduces properly both the total mass of the product as well as its increase with the velocity of flow and the inhomogeneity of the advanced front. The methodology used is simple and fast, and the numerical results presented here indicate its effectiveness. The use of macroscopic (continuous) models, although it has its limitations, is useful for quick and easy analysis of many phenomena.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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