

**SOLUTION APPROACH WITH GREEN'S FUNCTIONS FOR PREDICTING THE CONCENTRATION OF THE SLURRY WITHIN A STIRRED TANK REACTOR WITH NONLINEAR KINETICS**

**MÉTODO DE SOLUCIÓN CON FUNCIONES DE GREEN PARA PREDECIR LA CONCENTRACIÓN DE LODOS DENTRO DE UN REACTOR TANQUE AGITADO CON CINÉTICA NO LINEAL**

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**Abstract**

The purpose of this work is to set the basis for a numerical scheme to solve the model that describes the diffusion and reaction, with nonlinear kinetics, in the dispersed catalytic pellets part of the slurry contained in a reactor tank. The method presented is based on the use of Green's functions for the solution of the linear problem. However, different analytical solution approaches can lead to identical expressions for the solution; some of these results are compared and discussed. The numerical solution for the nonlinear case relies on the use of an iterative procedure. At this point, it is evident that the main drawback of the method proposed for the solution of the nonlinear transient problem is the infinite Fourier series that represent the Green's function. For such reason, the presented method is also used to obtain fluid and pellet concentration profiles for the quasi-steady state and steady-state cases. The resulting expressions for such two simpler cases are used to predict the concentration profiles that are also compared with those resulting from the numerical solution of the problem using finite differences. The good agreement of the predictions indicates that more compact expressions for the Green's function will improve the efficiency of the new numerical scheme.

*Keywords:* Green's function, analytical solution, iterative scheme, nonlinear kinetics, stirred tank reactor.

**Resumen**

El propósito de este trabajo es sentar las bases de un esquema numérico para resolver el modelo que describe la difusión y reacción, con cinética no lineal, en la parte del lodo que contiene pellets catalíticos dispersos en un reactor tanque agitado. El método presentado se basa en el uso de funciones de Green para la solución del problema lineal. Sin embargo, diferentes métodos de solución analítica pueden llevar a expresiones idénticas de la solución; algunos de estos métodos son comparados y discutidos. La solución numérica del caso no lineal se basa en el uso de un procedimiento iterativo. En este punto, es evidente que la principal desventaja del método propuesto para la solución del problema no lineal transitorio son las series de Fourier infinitas que representan a la función de Green. Por estas razones, el método presentado es usado también para obtener los perfiles de concentración en el fluido y las partículas para los casos de estados cuasi-estacionario y estacionario. Las expresiones resultantes para estos casos más simples se usan para predecir los perfiles de concentración que son comparados con los resultantes de la solución numérica usando diferencias finitas. La buena concordancia de las predicciones indica que expresiones más compactas para las funciones de Green mejorarán la eficiencia del esquema numérico.

*Palabras clave:* funciones de Green, solución analítica, método iterativo, cinética no lineal, reactor tanque agitado.

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## 1 Introduction

Several experimental systems that include a stirred tank reactor are often used to collect concentration data from which kinetic parameters are obtained (*cf.*, Smith, 1981). Furthermore, research in many anaerobic systems for hydrogen production are carried out in this type of systems (Fan, *et al.*, 2006). As a matter of fact, bio-hydrogen production from food waste requires optimizing hydraulic retention times in continuous stirred tank reactors (CSTR) (Reungsanga *et al.*, 2013). Nowadays, continuously stirred tank bioreactors are actively used for the treatment of hydrocarbon-rich wastewater from industrial wastewater effluents (Gargouri *et al.*, 2011). In addition, optimization and control of biogas production is studied in this type of reaction systems operating both as a single unit (Castrillón *et al.*, 2013) or in series (Boe and Angelidaki, 2009).

Modeling of most of the above mentioned applications requires the solution of the diffusion equation that governs transport and reaction processes in pellets that are in the mixed fluid. Even under isothermal conditions the model can be nonlinear due to the reaction rate kinetic expression. As consequence, even with all the recent advances in numerical methods and commercial software, different, more accurate and efficient numerical methodologies are being evaluated. One possibility is to derive schemes involving Green's functions and take advantage of the integral form to set numerical schemes with element discretization (Álvarez-Ramírez *et al.*, 2007). Iterative schemes for the solution of nonlinear reaction-diffusion problems in 1D were successfully applied by Valdés-Parada *et al.* (2007, 2008a) under isothermal and nonisothermal conditions. This approach was later extended to study reaction-diffusion-convection processes in tubular reactors by Valdés-Parada *et al.* (2008b) and Hernández-Martínez *et al.* (2011a). The idea in the iterative scheme is to regard the reaction rate term as a source in the differential equation, so that the Green's function only accounts for transport processes. The result is an implicit integral expression for the concentration that exhibits faster convergence rates than typical finite-differences schemes.

Kim *et al.* (2008) proposed to use 1D Green's functions associated to each coordinate axis to solve multi-dimensional second-order elliptic partial differential equations. Recently, Mandaliya *et al.* (2013) showed that two-dimensional Green's functions lead to accurate effectiveness factors

predictions in 2D geometries. Mansur *et al.* (2009) developed a numerical solution algorithm to study linear and transient heat conduction equations based on discrete Green's functions, which are determined numerically using the finite element method. The numerical results were found to be in excellent agreement with the results provided from other numerical and analytical schemes. Furthermore, Green's function formulations have also been used to pose an approximation problem based on a domain decomposition to produce non-local finite differences schemes for both reaction-diffusion (Hernández-Martínez *et al.*, 2011b) and reaction-diffusion-convection (Hernández-Martínez *et al.*, 2013) processes.

In this work, we extend the use of integral equation formulations based on Green's functions to study the dynamics of the concentration of a reactant in a slurry CSTR operating under unsteady conditions. To this end, we first solve the linear model to compute the corresponding Green's function and we demonstrate that the resulting expression can also be obtained from the Laplace transform method as previously reported in the literature (Marroquín *et al.*, 2002; Sales-Cruz *et al.*, 2012). Later on, we use the iterative scheme referred above to predict the effluent concentration dynamics for a Michaelis-Menten-type reaction rate. The paper is organized as follows: The solution of the nonlinear problem using Green's functions is presented in Section 2. This solution is verified by means of the Laplace transform method as shown in Appendix B. With the aim of simplifying the expressions for the Green's functions involved in the solutions, we propose to use those associated to the problem solution assuming quasi-steady conditions for transport and reaction in the catalytic pellets as explained in Section 3. Later on, in Section 4, the new method expressions for the steady-state case and quasi-steady state are used to predict the concentration profiles and their evolution, which are compared with those resulting from numerically solving the problem using finite differences. Conclusions and potential extensions are provided at the end of the paper.

## 2 Problem statement and solution

### 2.1 Dimensionless model

Let us consider the system sketched in Fig. 1 consisting of a slurry CSTR involving a fluid phase and a dispersed phase (the catalytic pellets).

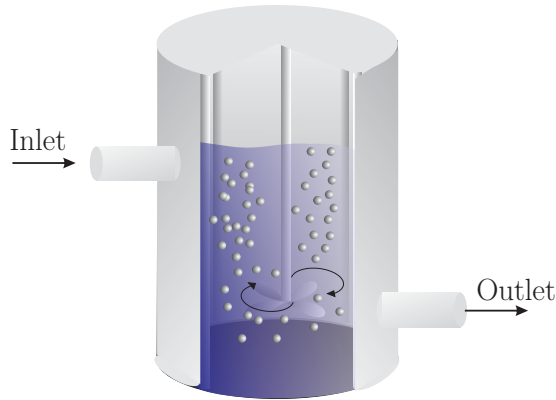


Fig. 1. Sketch of a slurry continuous stirred tank reactor.

The same fluid saturates the pores of the pellets, carrying a chemical reactive (species-A) that undergoes adsorption and chemical reaction at the surface of the pellet pores. From a previous work by Sales-Cruz *et al.* (2012), the following non-dimensional model can be used to describe mass transport, adsorption and reaction in the pellets:

$$\alpha \frac{\partial U_p}{\partial \tau} = \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial U_p}{\partial \xi} \right) - \Phi^2 R(U_p), \forall \xi \in (0, 1), \tau > 0 \quad (1)$$

In the above expression, the parameters  $\alpha$  and  $\Phi$  are associated to adsorption and the reaction rate, respectively (see Eq. 14b in Sales-Cruz, *et al.*, 2012). As a matter of fact,  $\Phi$  corresponds to the pellet Thiele modulus. In addition, the dimensionless time and radial coordinate are denoted by  $\tau$  and  $\xi$ , respectively. In this way,  $\xi = 0$  locates the center of the spherical catalytic pellet and  $\xi = 1$  its surface. Finally,  $U_p$  is the dimensionless concentration of species A in the pellets and  $R(U_p)$  is a nonlinear function of  $U_p$ . The concentration  $U_p$  is bound to be defined  $\forall \xi \in [0, 1]$ ; in addition,  $U_p$  is coupled with the concentration in the surrounding fluid,  $U_f$ , by the boundary condition

$$\xi = 1, \quad -\frac{\partial U_p}{\partial \xi} = Bi(U_p|_{\xi=1} - U_f) \quad (2)$$

with  $Bi$  being the Biot number and  $U_f$  solving the following differential equation

$$\frac{dU_f}{d\tau} = \psi_{in}(U_{in}(\tau) - U_f) + \psi_p(U_p|_{\xi=1} - U_f), \forall \tau > 0 \quad (3)$$

here, the parameters  $\psi_{in}$  and  $\psi_p$  represent the reciprocal of the dimensionless fluid residence time and a modified pellet Biot number, respectively (see

Eq. 15 in Sales-Cruz *et al.*, 2012). In addition,  $U_{in}$  is the inlet fluid concentration, which is assumed to be a known function of  $\tau$ . Finally, the initial conditions are

$$\text{when } \tau = 0, \quad U_p = U_{p0}; U_f = U_{f0} \quad (4)$$

The linear version of this problem has been solved by Marroquín *et al.* (2002) using the Laplace transform method and by Sales-Cruz *et al.* (2012) using a Fourier series expansion approach.

## 2.2 Solution approach in terms of Green's functions

Following the iterative scheme proposed by Valdés-Parada *et al.* (2007), the first step to find the solution is to state the governing initial and boundary-value problem for the Green's functions associated to the concentration in the pellets and in the fluid phase, *i.e.*,  $G_p^0$  and  $G_f^0$ , respectively. Recalling that, in this approach the reaction rate term is regarded as source in Eq. (1), the adjoint Green's functions,  $G_p^{0*}$  and  $G_f^{0*}$ , solve the following problem

$$-\alpha \frac{\partial G_p^{0*}}{\partial \tau} - \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial G_p^{0*}}{\partial \xi} \right) = \delta(\tau - \tau_0) \delta(\xi - \xi_0) \quad (5a)$$

$$\xi = 1, \quad -\frac{\partial G_p^{0*}}{\partial \xi} = Bi(G_p^{0*}|_{\xi=1} - G_f^{0*}) \quad (5b)$$

$$-\frac{dG_f^{0*}}{d\tau} \Big|_{\xi=1} = -\psi_{in} G_f^{0*}|_{\xi=1} + \psi_p(G_p^{0*}|_{\xi=1} - G_f^{0*}|_{\xi=1}) \quad (5c)$$

With initial conditions

$$G_p^{0*}(\xi, \xi_0, \tau - \tau_0) = 0, G_f^{0*}(\xi, \xi_0, \tau - \tau_0) = 0, \quad \tau > \tau_0 \quad (5d)$$

It should be noticed that the accumulation terms in Eqs. (5a) and (5c) have an opposite sign to the one corresponding to the problem for  $U_p$  and  $U_f$ , respectively; this is with the purpose of obtaining the following relationship between the associated Green's functions and their adjoints

$$G_j^0(\xi, \xi_0, \tau - \tau_0) = G_j^{0*}(\xi, \xi_0, \tau_0 - \tau), \quad j = p, f \quad (6)$$

The next step towards the solution is to use Green's formula in terms of the dependent variables  $U_p$  and  $G_p^{0*}$ ,

$$\int_{\xi=0}^{\xi=1} \left[ \frac{G_p^{0*}}{\xi^2} \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial U_p}{\partial \xi} \right) - \frac{U_p}{\xi^2} \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial G_p^{0*}}{\partial \xi} \right) \right] \xi^2 d\xi$$

$$= \left[ G_p^{0*} \frac{\partial U_p}{\partial \xi} - U_p \frac{\partial G_p^{0*}}{\partial \xi} \right]_{\xi=1} \quad (7)$$

Substitution of the corresponding differential equations and boundary conditions leads to

$$\int_{\xi=0}^{\xi=1} \left[ \alpha \frac{\partial G_p^{0*} U_p}{\partial \tau} + \Phi^2 G_p^{0*} R_p + U_p \delta(\tau - \tau_0) \delta(\xi - \xi_0) \right] \xi^2 d\xi$$

$$= Bi \left[ G_p^{0*} \Big|_{\xi=1} U_f - U_p \Big|_{\xi=1} G_f^{0*} \right] \quad (8)$$

In order to make further progress, let us integrate this equation from  $\tau = 0$  to  $\tau = \tau_0^+$  and the use of Dirac's delta function filtration property, followed by the change of variables  $\tau \rightleftharpoons \tau_0^+$ ,  $\xi_0 \rightleftharpoons \xi$  and  $G_j^{0*} \rightleftharpoons G_j^0$  ( $j = p, f$ ), in order to obtain

$$U_p(\xi, \tau) = \underbrace{\alpha U_{p0} \int_{\xi_0=0}^{\xi_0=1} G_p^0(\xi, \xi_0, \tau) \xi_0^2 d\xi_0}_{\text{influence of the initial concentration in the pellet}}$$

$$- \underbrace{\Phi^2 \int_{\tau_0=0}^{\tau_0=\tau} \int_{\xi_0=0}^{\xi_0=1} [G_p^0(\xi, \xi_0, \tau - \tau_0) R_p] \xi_0^2 d\xi_0 d\tau_0}_{\text{influence of the reaction rate}}$$

$$+ \underbrace{\int_{\tau_0=0}^{\tau_0=\tau} Bi \left[ G_p^0 \Big|_{\xi_0=1} U_f - U_p \Big|_{\xi_0=1} G_f^0(\xi, 1, \tau - \tau_0) \right] d\tau_0}_{\text{influence of the mass exchange with the fluid}} \quad (9)$$

where the physical meaning of each term has been clearly identified. The above result has the drawback that it is expressed in terms of the concentration in the fluid phase, which is not known at this point. To overcome this issue, let us integrate the combination of the fluid equations, Eqs. (3) and (5c), and perform similar algebraic steps as those used above, to arrive to the following result

$$- \frac{Bi}{\psi_p} U_{f0} G_f^0 \Big|_{\tau_0=0, \xi_0=1} = \int_{\tau_0=0}^{\tau_0=\tau} \frac{Bi}{\psi_p} \psi_{in} G_f^0 \Big|_{\xi_0=1} U_{in}(\tau_0) d\tau_0$$

$$+ \int_{\tau_0=0}^{\tau_0=\tau} Bi \left( G_f^0 U_p \Big|_{\xi_0=1} - U_f G_p^0 \Big|_{\xi_0=1} \right) d\tau_0 \quad (10)$$

Addition of Eqs. (9) and (10) leads to

$$U_p(\xi, \tau) = \underbrace{\alpha U_{p0} \int_{\xi_0=0}^{\xi_0=1} G_p^0(\xi, \xi_0, \tau) \xi_0^2 d\xi_0}_{\text{influence of the initial concentration in the pellet}}$$

$$+ \underbrace{Bi U_{f0} \frac{1}{\psi_p} G_f^0 \Big|_{\tau_0=0}}_{\text{influence of the initial concentration in the fluid}}$$

$$+ \underbrace{Bi \psi_{in} \int_{\tau_0=0}^{\tau_0=\tau} \frac{1}{\psi_p} G_f^0 U_{in}(\tau_0) d\tau_0}_{\text{influence of the inlet fluid concentration}}$$

$$- \underbrace{\Phi^2 \int_{\tau_0=0}^{\tau_0=\tau} \int_{\xi_0=0}^{\xi_0=1} [G_p^0(\xi, \xi_0, \tau - \tau_0) R_p(\xi_0)] \xi_0^2 d\xi_0 d\tau_0}_{\text{influence of the reaction rate}} \quad (11)$$

Comparing Eqs. (9) and (11), it is clear that the influence of mass exchange with the fluid phase gave rise to two terms accounting for the influence of the initial concentration in the fluid phase and of the inlet concentration to the tank. Since Eq. (11) is now independent of  $U_f$ , it can be regarded as the desired solution for the concentration in the pellets. Therefore, we may evaluate it at  $\xi = 1$  and also take the first derivative with respect to  $\xi$  evaluated at the same point and substitute the resulting expressions into the interfacial boundary condition (Eq. 2), to obtain the corresponding expression for  $U_f$ , which is given by

$$U_f(\tau) = \underbrace{\alpha U_{p0} \int_{\xi_0=0}^{\xi_0=1} G_f^0(1, \xi_0, \tau) \xi_0^2 d\xi_0}_{\text{influence of the initial concentration in the pellet}}$$

$$+ \underbrace{U_{f0} Bi H^0(1, 1, \tau)}_{\text{influence of the initial concentration in the fluid}}$$

$$\begin{aligned}
 & + \underbrace{Bi \psi_{in} \int_{\tau_0=0}^{\tau_0=\tau} H^0(1, 1, \tau - \tau_0) U_{in}(\tau_0) d\tau_0}_{\text{influence of the inlet fluid concentration}} \\
 & - \underbrace{\Phi^2 \int_{\tau_0=0}^{\tau_0=\tau} \int_{\xi_0=0}^{\xi_0=1} G_f^0(\xi, \xi_0, \tau - \tau_0) R_p(\xi_0) \xi_0^2 d\xi_0 d\tau_0}_{\text{influence of the reaction rate in the pellet}}
 \end{aligned} \tag{12}$$

For the sake of brevity in presentation, we introduced

$$H^0(\xi, \xi_0, \tau - \tau_0) = \frac{1}{\psi_p} \left[ G_f^0 + \frac{1}{Bi} \frac{\partial G_f^0}{\partial \xi} \right]_{(\xi, \xi_0, \tau - \tau_0)} \tag{13}$$

Clearly Eqs. (11) and (12) share similar structures and we will refer to them as the formal solutions of the dimensionless problem given by Eqs. (1)-(10). The concentration profiles and associated variables can be obtained by the iterative solution of the mentioned expressions. However, such evaluation requires the associated Green's functions to the linear original problem in the absence of bulk reaction (*i.e.*,  $\Phi = 0$ ),  $G_p^0(\xi, \xi_0, \tau - \tau_0)$  and  $G_f^0(\xi, \xi_0, \tau - \tau_0)$ . The procedure to obtain them using Fourier series expansions is outlined in Appendix A; it suffices here to provide the resulting expressions, which are

$$G_p^0(\xi, \xi_0, \tau - \tau_0) = \sum_{n=1}^{\infty} \frac{\varphi_n(\xi_0) \varphi_n(\xi)}{K_n} e^{-\lambda_n^2 \alpha^{-1}(\tau - \tau_0)} \tag{14a}$$

$$G_f^0(\xi, \xi_0, \tau - \tau_0) = \psi_p \sum_{n=1}^{\infty} \frac{\varphi_n(\xi_0) \varphi_n(\xi) e^{-\lambda_n^2 \alpha^{-1}(\tau - \tau_0)}}{K_n (\psi_p + \psi_{in} - \lambda_n^2 \alpha^{-1})} \tag{14b}$$

Certainly, the derivation of Eqs. (11) and (12) could have been performed using other solution approaches such as the Laplace transform method. In Appendix B we demonstrate that the expressions provided above can be recovered with this method.

At this point, it should be clear that the evaluation of the Fourier series representing the Green's functions will require significant amounts of computing time. For such reason, we are currently looking for expressions of the associated Green's functions that allow a more efficient calculation procedure. Nevertheless, it is valuable to determine

if the presented methodology leads to reasonable predictions for other simpler cases that keep the two coupled governing equations structure of the nonlinear problem. This can be achieved by assuming that transport and reaction in the pellets take place under quasi-steady conditions as detailed in the following paragraphs.

### 3 Nonlinear quasi-steady and steady-state solution

#### 3.1 Quasi-steady solution

As explained above, with the aim of avoiding the computational burden of using the Green's functions for the fully transient problem in the iterative scheme for computing the concentration dynamics, we direct our attention to the case in which transport and reaction in the pellets can be assumed to be quasi-steady. Such conditions can be determined by performing an order of magnitude analysis to Eq. (1) to conclude that quasi-steady conditions can be achieved for  $\tau \gg \alpha$ , or, in terms of dimensional quantities,

$$\frac{r_p^2}{D_w} \left( 1 + \frac{a_{vw} K}{\varepsilon \gamma \omega} \right) \ll t \tag{15}$$

where  $D_w$  and  $K$  are the effective diffusion coefficient and adsorption rate in the pellets, respectively; whereas  $a_{vw}$ ,  $\varepsilon \gamma \omega$  and  $r_p$  refer to the interfacial area per unit volume, porosity and pellet radius, respectively. Under these conditions, the accumulation term in the differential equation for the concentration in the pellet (Eq. 1) can be neglected and this equation takes the form

$$\frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial U_p^{qs}}{\partial \xi} \right) - \Phi^2 R_p = 0, \quad \text{for } 0 < \xi < 1 \tag{16}$$

and the rest of the problem formulation remains unaltered. Using the integral equation formulation based on the use of Green's functions applied above, it is possible to solve the quasi-steady-state problem to find

$$\begin{aligned}
 U_p^{qs}(\xi, \tau) & = U_{f0} e^{-\psi_{in} \tau} + \psi_{in} \int_{\tau_0=0}^{\tau_0=\tau} U_{in}(\tau_0) e^{-\psi_{in}(\tau - \tau_0)} d\tau_0 \\
 & - \Phi^2 \int_{\tau_0=0}^{\tau_0=\tau} \int_{\xi_0=0}^{\xi_0=1} [G_p^{qs}(\xi_0, \xi, \tau - \tau_0) R_p(U_p^{qs}(\xi_0, \tau_0))] \xi_0^2 d\xi_0 d\tau_0
 \end{aligned} \tag{17a}$$

$$\begin{aligned}
 U_f^{qs}(\tau) &= U_{f0} e^{-\psi_m \tau} + \psi_{in} \int_{\tau_0=0}^{\tau_0=\tau} U_{in}(\tau_0) e^{-\psi_m(\tau-\tau_0)} d\tau_0 \\
 &- \Phi^2 \int_{\tau_0=0}^{\tau_0=\tau} \int_{\xi_0=0}^{\xi_0=1} \left[ G_f^{qs}(1, \xi_0, \tau - \tau_0) R_p(U_p^{qs}(\xi_0, \tau_0)) \right] \xi_0^2 d\xi_0 d\tau_0
 \end{aligned}
 \tag{17b}$$

Comparing these expressions with those obtained in the previous section (Eqs. 2.2), we notice that the influence of the initial condition in the pellets is no longer present. In addition, the Green's functions  $G_p^{qs}$  and  $G_f^{qs}$  solve Eqs. (5) with Eq. (5a) written under quasi-steady conditions. The resulting expressions from solving that problem are

$$G_p^{qs}(\xi, \xi_0, \tau - \tau_0) = \frac{1}{Bi} \begin{cases} (Bi\xi_0^{-1} + 1 - Bi) \delta(\tau - \tau_0) + \psi_p e^{-\psi_m(\tau-\tau_0)}, & \text{for } 0 < \xi < \xi_0 \\ (Bi\xi^{-1} + 1 - Bi) \delta(\tau - \tau_0) + \psi_p e^{-\psi_m(\tau-\tau_0)}, & \text{for } \xi_0 < \xi < 1 \end{cases}
 \tag{18a}$$

$$G_f^{qs}(\tau - \tau_0) = \frac{\psi_p}{Bi} e^{-\psi_m(\tau-\tau_0)}
 \tag{18b}$$

Certainly, these expressions are easier to evaluate than those given by Eqs. (14) and will be used in the iterative scheme to predict the concentration dynamics in the tank. At this point one may ponder about the predictive capabilities of the quasi-steady solution with respect to the fully transient solution. This issue was discussed by Valdés-Parada *et al.* (2005). These authors concluded that the quasi-steady-state solution is a very convenient tool to estimate the dynamics of the fluid, average and interfacial concentrations, since the predictions exhibited a difference smaller than 10% with those resulting from the fully-transient solution. Furthermore, it is worth stressing that the quasi-steady state assumption is not exclusive to this type of systems. As a matter of fact, the quasi-steady assumption is a reliable tool for studying mass transport in biological and synthetic membranes as explained by Truskey *et al.* (2009). For *in vitro* enzyme-catalyzed reactions, described by the Michaelis-Menten model, experiments are usually carried out under conditions of substrate excess (or, equivalently, when the enzyme concentration is sufficiently small) in order to guarantee quasi-steady conditions and thus justifying the Briggs-Haldane approximation (Tzafirri and Edelman, 2007).

Moreover, Pedersen *et al.* (2008) extended the use of the quasi-steady condition to study complex enzyme reactions such as competitive reactions, double phosphorylation, Goldbeter-Koshland switch. Recently, Kim *et al.* (2014) provided an interesting discussion about the separation of time scales justifying the deterministic and stochastic versions of the quasi-steady condition for simulating biochemical reaction networks with disparate timescales.

### 3.2 Steady-state solution

As a final part of the solution procedure, it is illustrative to provide the corresponding expressions for the concentration in the pellets and in the fluid under steady-state conditions. Following the same solution procedure used above, one may solve the steady-state version of Eqs. (1)-(3) and obtain

$$U_p^{ss}(\xi) = U_{in} - \Phi^2 \int_{\xi_0=0}^{\xi_0=1} \left[ G_p^{ss}(\xi, \xi_0) R_p(U_p^{ss}(\xi_0)) \right] \xi_0^2 d\xi_0
 \tag{19a}$$

$$U_f^{ss} = U_{in} - \Phi^2 \int_{\xi_0=0}^{\xi_0=1} G_f^{ss}(1, \xi_0) R_p(U_p^{ss}(\xi_0)) \xi_0^2 d\xi_0
 \tag{19b}$$

where the influences of the initial condition in the fluid and in the pellets are no longer present and the inlet function is no longer a function of time. Indeed, the above expressions could have resulted from taking  $\tau \gg 1$  in Eqs. (2.2) or in Eqs. (17). In this case, the steady-state versions of the Green's functions are

$$G_p^{ss}(\xi, \xi_0) = \begin{cases} \xi_0^{-1} + \frac{(1-Bi)\psi_m + \psi_p}{Bi\psi_m}, & \text{for } 0 < \xi < \xi_0 \\ \xi^{-1} + \frac{(1-Bi)\psi_m + \psi_p}{Bi\psi_m}, & \text{for } \xi_0 < \xi < 1 \end{cases}
 \tag{20a}$$

$$G_f^{ss} = \frac{\psi_p}{Bi\psi_m}
 \tag{20b}$$

Despite the simplicity of these expressions, they will prove to be quite useful in carrying out a parametric analysis of the model, as will be shown in the following section.

## 4 Results

In this section, the numerical results from the implicit formulas derived in this paper are compared with the predictions resulting of a classical finite difference

approach. The nonlinear kinetic expression used in all test is a Michaelis-Menten type given by

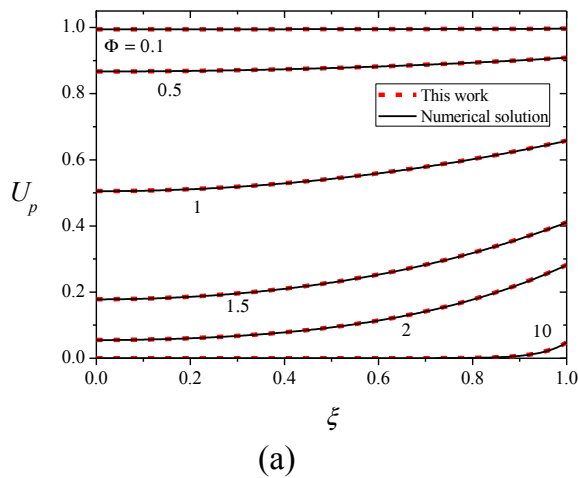
$$R(U_p) = \frac{(1 + \gamma)^2 U_p}{(1 + \gamma U_p)^2} \quad (21)$$

Without any loss of generality, in all numerical simulation the parameter  $\gamma$  was set equal to the unity. In order to evaluate the steady-state analytical solution, we used the following iterative approach:

1. For a given set of parameters ( $Bi, \Phi, \psi_{in}, \psi_p$  and tolerance), assume the concentration fields.
2. Compute the Green's functions  $G_p^{ss}$  and  $G_f^{ss}$  using Eqs. (20).
3. Compute the integral terms on the RHS of Eqs. (19).
4. Compute  $U_p^{ss}$  and  $U_f^{ss}$  using Eqs. (19).
5. Verify if the convergence criterion is met, if this is the case, report the solution; otherwise improve the assumption of the concentration fields and return to step 3.

In all the computations we chose as a convergence criterion the relative error percent in the predictions of the average particle concentration with respect to the value resulting from the concentration fields of the previous iteration. The average particle concentration is defined as

$$\langle U_p \rangle = 3 \int_{\xi=0}^{\xi=1} U_p \xi^2 d\xi \quad (22)$$



All the results were obtained fixing the tolerance to  $10^{-8}$ . The numerical solution of the problem was performed using finite differences schemes following a similar approach to the one detailed above for the analytical solution with the same convergence criterion.

In Fig. 2, we evaluate the influence of the reaction rate and interfacial mass transport over the steady-state concentration profiles in the catalytic pellets. As expected, when the reaction rate is larger than the rate of diffusion (*i.e.*, as the Thiele modulus increases) the concentration decreases. This effect is more drastic for  $\Phi > 1$  as shown in Fig. 2a. In addition, if one fixes the Thiele modulus and modifies the Biot number, it turns out that the results are more sensitive to variations in  $Bi$  when this parameter is lower than one. The comparison with the finite difference predictions is excellent.

In Fig. 3 we extend the analysis of the influence of the Biot number and the Thiele modulus over the fluid phase concentration as well as over the interfacial concentration and the average concentration. As expected, all the concentrations decrease as the reaction rate becomes faster than diffusion. Since transport of species  $A$  goes from the fluid phase to the catalytic pellets, it is to be expected that  $\langle U_p \rangle < U_p|_{\xi=1} < U_f$ . Consistently with the results provided in Fig. 2, for  $\Phi > 1$ , we can appreciate that small variations in  $\Phi$  translate to rapid reductions in the concentration values.

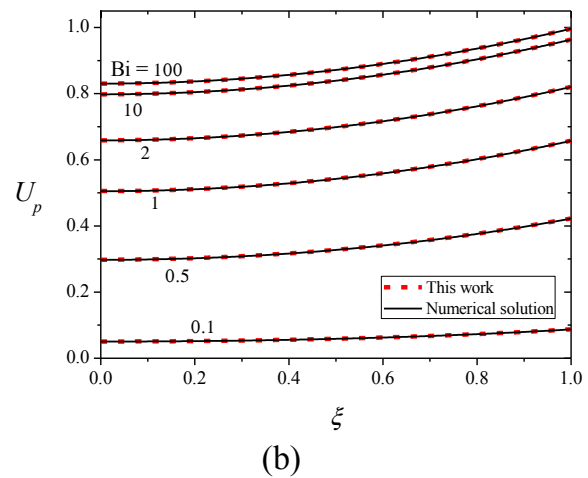


Fig. 2. Effect of Thiele modulus and Biot number on the pellet steady-state concentration profiles. a) Variations on the Thiele modulus for  $Bi = 1$ , and b) Variations on the Biot for  $\Phi = 1$ .

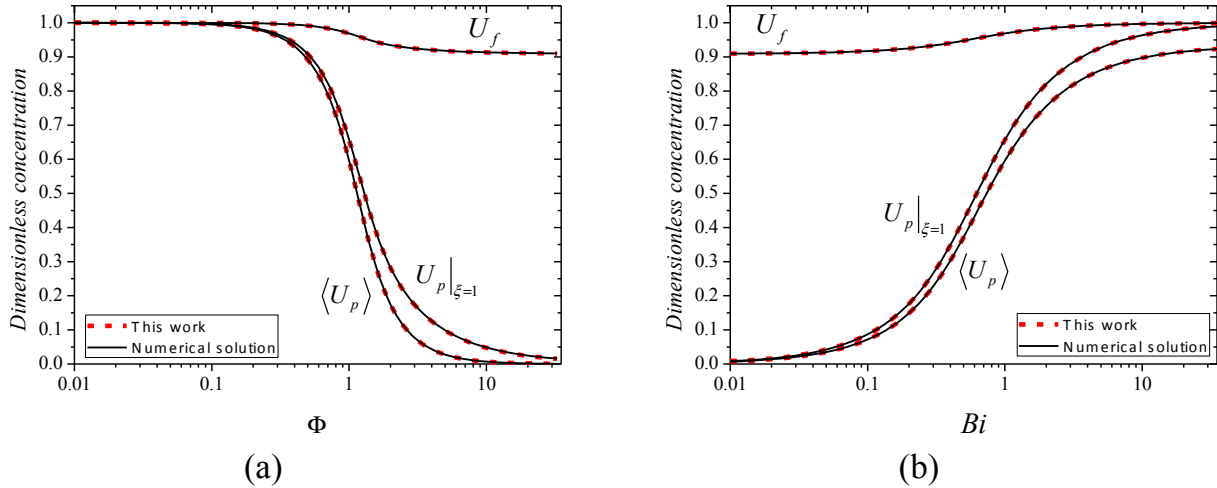


Fig. 3. Effect of Thiele modulus and Biot number on fluid steady-state concentration profiles. a) Variations of Thiele modulus and  $Bi = 1$  and b) Variations of Biot for  $\Phi = 1$ .

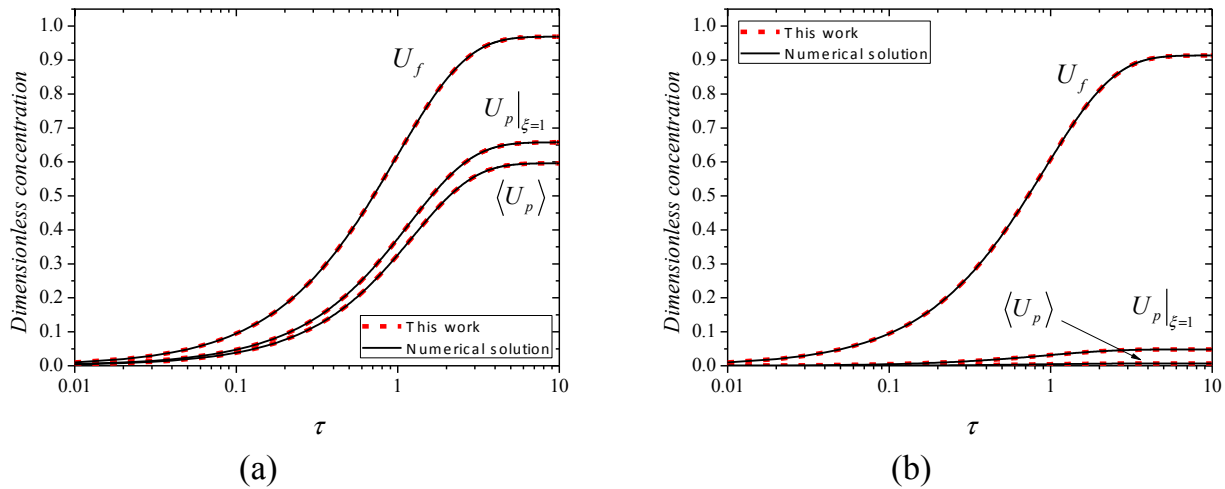


Fig. 4. Time evolution of fluid quasi-steady-state concentration for  $Bi = 1$ . a)  $\Phi = 1$  and b)  $\Phi = 10$ .

In addition, the predictions of all the concentrations are more sensitive for Biot number values around the unity. Comparison of the predictions from the analytical and numerical solutions again shows great agreement. As a matter of fact, the % of difference between both solutions is below  $10^{-4}$  %.

Directing the attention to the dynamics of  $\langle U_p \rangle$ ,  $U_p|_{\xi=1}$  and  $U_f$ , we evaluated the quasi-steady state solutions using the iterative scheme outlined above. The main difference is that the iteration is performed at each time step. To carry put the simulations, we fixed the initial conditions in the fluid phase and in the particles to be zero and the inlet concentration was set

to be a unit step function,

$$U_{in}(\tau) = \begin{cases} 1, & \tau \geq \tau_0 \\ 0, & \tau < \tau_0 \end{cases} \quad (23)$$

Certainly other inlet time functions could be considered such as a finite pulse function and a periodic function as shown in previous studies (*cf.*, Marroquín *et al.*, 2002; Valdés-Parada *et al.*, 2005). In all the simulations, different time steps were used in order to guarantee that the solution is independent of this numerical parameter. In Fig. 4 we show the evolution of the fluid, pellet surface and pellet average concentration for a case when the fluid mass transfer resistance is not negligible (*i.e.*,  $Bi = 1$ ).



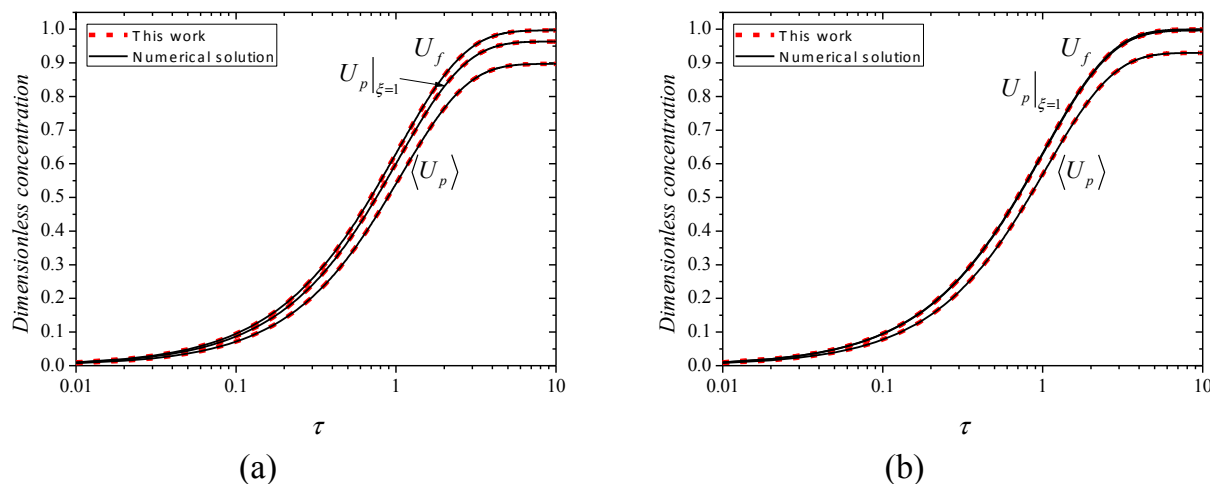


Fig. 5. Time evolution of fluid quasi-steady-state concentration for  $\Phi = 1$ . a)  $Bi = 10$  and b)  $Bi = 100$ .

The analysis is provided for two cases: a) The characteristic times of diffusion and reaction are comparable (*i.e.*,  $\Phi = 1$ ) and b) The diffusive resistance controls the process (*i.e.*,  $\Phi = 10$ ). Since the Biot number is fixed, the differences between  $\langle U_p \rangle$  and  $U_p|_{\xi=1}$  are maintained in the plots provided in Figs. 4a and 4b. Clearly, increasing the Thiele modulus from 1 to 10 affected more drastically the concentration values in the pellets, while the dynamics of the concentration in the fluid was almost unaffected. Finally, in Fig. 5 we show the effect of the fluid mass transfer resistance on the evolution of the three mentioned concentrations for a moderate Thiele modulus value. In this case we appreciate that the interfacial concentration matches the fluid-phase concentration for  $Bi \geq 10$  for all times. In all cases the agreement between the analytical and numerical solutions is quite close as the % of difference between the solutions remained on the order of  $10^{-4}$  or less for all times.

## Final remarks

In this work we developed the analytical solution for the prediction of the concentration dynamics in a slurry stirred tank reactor. The solution of the fully transient model was carried out using integral equation formulations based on Green's functions. The physical meaning of the several terms in the solutions was clearly identified. While the formulation based on Green's functions is both mathematically and physically appealing, it is worth remarking that it is not the only way to obtain the solution as shown

in Appendix B using the Laplace transform method in combination with the method of eigenfunction expansions. The demonstration is interesting *per se*, since the concentration formulas in the Laplace domain can be useful for frequency analysis.

Since the Green's functions for the fully transient model are not easy to evaluate in terms of computer time, we evaluated the quasi-steady and steady-state solutions and used an iterative approach to predict the values of the concentration in both the particle and in the fluid. The comparison of the predictions obtained with the equations based on Green's functions indicates that the methodology is just as good as other well-established methods. The analysis was focused on the influence of the reaction rate and interfacial transport resistances over the steady-state concentration profiles and their dynamics. One possibility to avoid the infinity Fourier series representation, is to combine the quasi-steady state Green's functions with some special form of them for a short period of time after the start-up of the process. These ideas will be further explored in another work.

## Acknowledgments

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## Nomenclature

$Bi$  pellet Biot number

$C_n(\tau)$	Fourier series coefficient for Green's functions
$G$	Green's function for passive case
$h_n(\xi)$	fluid Eigen function
$R_p$	dimensionless reaction rate
$s$	Laplace parameter
$U_p$	dimensionless pellet concentration
$U_f$	dimensionless fluid concentration
<i>Greek symbols</i>	
$\alpha$	pellet adsorption parameter
$\delta$	Dirac's delta function
$\Phi$	pellet Thiele modulus
$\varphi_n(\xi)$	pellet Eigen function
$\lambda_n$	$n$ th-Eigen value
$\xi$	dimensionless radial coordinate of the spherical particles
$\psi_{in}$	inverse of the dimensionless residence time
$\psi_p$	modified pellet Biot number
$\tau$	dimensionless time
<i>Subscripts</i>	
$f$	fluid
$p$	pellet
0	indicates reference value, source point or time
<i>Subscripts</i>	
0	no chemical reaction
qs	quasi steady state
ss	steady state

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## Appendix A Derivation of the unsteady Green's functions using Fourier series

In this section we derive the analytical expressions of the Green's functions  $G_p^0(\xi, \xi_0, \tau - \tau_0)$  and  $G_f^0(\xi, \xi_0, \tau - \tau_0)$  using Fourier series. The governing equations for these dependent variables are given by Eqs. (5). In those equations, two modifications are needed: a) the sign in the three time derivatives must be changed to the opposed sign, and b) the initial conditions are given by

$$G_p^0(\xi, \xi_0, \tau - \tau_0) = 0, \quad G_f^0(\xi, \xi_0, \tau - \tau_0) = 0, \quad \tau < \tau_0 \quad (\text{A.1})$$

We propose to obtain the Green's functions in the form of the following Fourier series expansions

$$G_p^0 = \sum_{n=1}^{\infty} C_n(\tau) \varphi_n(\xi) \quad \text{and} \quad G_f^0 = \sum_{n=1}^{\infty} C_n(\tau) h_n(\xi) \quad (\text{A.2})$$

where the Eigen functions are given by

$$\varphi_n(\xi) = \frac{\sin(\lambda_n \xi)}{\xi} \quad (\text{A.3a})$$

$$h_n(1) = \frac{\varphi_n(1) \psi_p}{(\psi_p + \psi_{in} - \lambda_n^2 \alpha^{-1})} \quad (\text{A.3b})$$

These are the solution of the associated Sturm-Liouville problem that is defined by the following differential and algebraic equations

$$\frac{1}{\xi^2} \frac{d}{d\xi} \left( \xi^2 \frac{d\varphi_n}{d\xi} \right) = -\lambda_n^2 \varphi_n \quad (\text{A.4a})$$

$$-\psi_{in} + \psi_p \left( \frac{\varphi_n(1)}{h_n} - 1 \right) = - \left( \frac{\Phi^2 + \lambda_n^2}{\alpha} \right) \quad (\text{A.4b})$$

which are coupled by the interfacial boundary condition

$$\xi = 1, \quad -\varphi_n'(1) = Bi [\varphi_n(1) - h_n(1)] \quad (\text{A.4c})$$

This problem can be obtained by applying the method of separation of variables to the boundary value problem that defines  $G_p^0(\xi, \xi_0, \tau - \tau_0)$  and  $G_f^0(\xi, \xi_0, \tau - \tau_0)$ . Furthermore, the Eigen values,

$\lambda_n$  are obtained by solving the following algebraic equation

$$\frac{\tan \lambda_n}{\lambda_n} = \frac{\psi_p + \psi_{in} - \lambda_n^2 \alpha^{-1}}{(\lambda_n^2 \alpha^{-1} - \psi_{in})(Bi - 1) + \psi_p} \quad \text{for } n = 1, 2, 3, \dots \infty \quad (\text{A.5})$$

and the orthogonality condition is given by

$$\alpha \int_{\xi=0}^{\xi=1} \varphi_n \varphi_m \xi^2 d\xi + \frac{Bi}{\psi_p} h_m h_n = 0, \quad \text{for } n \neq m \quad (\text{A.6})$$

In order to find the coefficients  $C_n(\tau)$  in Eqs. (A.2), let us write Green's formula in terms of the functions  $G_p^0$  and  $\varphi_m$ ,

$$\int_{\xi=0}^{\xi=1} \left[ \varphi_m \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial G_p^0}{\partial \xi} \right) - \frac{G_p^0}{\xi^2} \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial \varphi_m}{\partial \xi} \right) \right] \xi^2 d\xi = \left[ \varphi_m \frac{\partial G_p^0}{\partial \xi} - G_p^0 \frac{\partial \varphi_m}{\partial \xi} \right]_{\xi=1} \quad (\text{A.7})$$

which, after incorporation of the differential equations and the boundary conditions, takes the form

$$\int_{\xi=0}^{\xi=1} \left[ \varphi_m \left( \frac{\partial G_p^0}{\partial \tau} - \delta(\tau - \tau_0) \delta(\xi - \xi_0) \right) + \lambda_m^2 \varphi_m G_p^0 \right] \xi^2 d\xi = Bi \left[ \varphi_m(1) G_f^0 - h_m G_p^0 \right]_{\xi=1} \quad (\text{A.8})$$

Application of the filtration property of Dirac's delta function, after some algebra involving the fluid equations, leads to

$$\alpha \int_{\xi=0}^{\xi=1} \varphi_m \left( \frac{\partial G_p^0}{\partial \tau} + \lambda_m^2 \alpha^{-1} G_p^0 \right) \xi^2 d\xi = \varphi_m(\xi_0) \delta(\tau - \tau_0) - \frac{Bi h_m}{\psi_p} \left( \frac{dG_f^0}{d\tau} + \lambda_m^2 \alpha^{-1} G_f^0 \right) \quad (\text{A.9})$$

To make further progress, let us substitute the expressions for  $G_p^0$  and  $G_f^0$  given in Eqs. (A.2) and take into account the orthogonality condition (Eq. A.6), in order to obtain the following linear first-order differential equation,

$$\frac{dC_n}{d\tau} + \lambda_m^2 \alpha^{-1} C_n = \frac{\varphi_n(\xi_0)}{K_n} \delta(\tau - \tau_0) \quad (\text{A.10})$$

where, for convenience, we introduced

$$K_n = \alpha \int_0^1 \xi^2 \varphi_n^2 d\xi + \frac{Bi h_n^2}{\psi_p} \quad (\text{A.11})$$

Time-integration of Eq. (A.10) from  $\tau = 0$  to  $\tau = \tau_0^+$  and taking into account that, in order to satisfy Eq. (A.1), it follows that  $C_n(0) = 0$ , yields the expression for the coefficients  $C_n(\tau)$ , which together with Eqs. (A.2) leads to

$$G_p^0(\xi, \xi_0, \tau - \tau_0) = \sum_{n=1}^{\infty} \frac{\varphi_n(\xi_0) \varphi_n(\xi)}{K_n} e^{-\lambda_n^2 \alpha^{-1} (\tau - \tau_0)} \quad (\text{A.12a})$$

$$G_f^0(\xi, \xi_0, \tau - \tau_0) = \psi_p \sum_{n=1}^{\infty} \frac{\varphi_n(\xi_0) \varphi_n(\xi)}{K_n (\psi_p + \psi_{in} - \lambda_n^2 \alpha^{-1})} e^{-\lambda_n^2 \alpha^{-1} (\tau - \tau_0)} \quad (\text{A.12b})$$

## Appendix B Solution by the Laplace transform method

In this section, we show that the expressions given by Eqs. (11) and (12) can be derived by other methodologies, in this case we use the Laplace transform method combined with variation of parameters to solve the resulting differential equation. After a lengthy procedure, that includes the application of the interfacial boundary condition, the following equations for the Laplace transform of the particle and fluid concentrations  $\bar{U}_p(\xi, s)$  and  $\bar{U}_f(s)$ , are obtained

$$\begin{aligned} \bar{U}_p(\xi, s) = & \frac{U_{p0}}{s} - \frac{Bi U_{p0}}{s [\beta \cosh(\beta) + (Bi - 1) \sinh(\beta)]} \frac{\sinh(\beta \xi)}{\xi} \\ & + U_{p0} \frac{\psi_p Bi}{s \beta M(0, s)} \left[ \frac{\beta \cosh(\beta) - \sinh(\beta)}{\beta \cosh(\beta) + (Bi - 1) \sinh(\beta)} \right] \frac{\sinh(\beta \xi)}{\xi} \\ & + U_{f0} \frac{Bi}{\beta M(0, s)} \frac{\sinh(\beta \xi)}{\xi} + \bar{U}_{in} \frac{\psi_{in} Bi}{\beta M(0, s)} \frac{\sinh(\beta \xi)}{\xi} \\ & + \frac{Bi \psi_p}{\beta M(0, s)} \frac{\sinh(\beta \xi)}{\xi} \bar{\mathcal{R}}_p(1) + \bar{\mathcal{R}}_p(\xi) \end{aligned} \quad (\text{B.1a})$$

$$\begin{aligned} \bar{U}_f(s) = & U_{p0} \frac{\psi_p [\beta \cosh(\beta) - \sinh(\beta)]}{s \beta M(0, s)} \\ & + \frac{\beta \cosh(\beta) + (Bi - 1) \sinh(\beta)}{\beta M(0, s)} U_{f0} \\ & + \psi_{in} \frac{\beta \cosh(\beta) + (Bi - 1) \sinh(\beta)}{\beta M(0, s)} \bar{U}_{in} \end{aligned}$$

$$+ \frac{\psi_p \bar{\mathcal{R}}_p(1) [\beta \cosh(\beta) + (Bi - 1) \sinh(\beta)]}{\beta M(0, s)} \quad (\text{B.1b})$$

here we used the following definitions

$$\beta = \sqrt{\alpha s} \quad (\text{B.2a})$$

$$\begin{aligned} \bar{\mathcal{R}}_p(\xi) = & -\frac{\Phi^2 \cosh(\beta \xi)}{\beta} \frac{1}{\xi} I_S(\xi, 0) + \frac{\Phi^2 \sinh(\beta \xi)}{\beta} \frac{1}{\xi} I_C(\xi, 1) \\ & + \frac{\Phi^2 \sinh(\beta \xi)}{\beta} \frac{1}{\xi} \left[ \frac{\beta \sinh(\beta) + (Bi - 1) \cosh(\beta)}{\beta \cosh(\beta) + (Bi - 1) \sinh(\beta)} \right] I_S(1, 0) \end{aligned} \quad (\text{B.2b})$$

$$I_S(\xi, 0) = \int_{\zeta=0}^{\zeta=\xi} \zeta \sinh(\beta \zeta) \bar{R}_p d\zeta \quad (\text{B.2c})$$

$$I_C(\xi, 1) = \int_{\zeta=1}^{\zeta=\xi} \zeta \cosh(\beta \zeta) \bar{R}_p d\zeta \quad (\text{B.2d})$$

$$\begin{aligned} \beta M(\xi, s) = & (s + \psi_{in} + \psi_p) \beta \cosh[\beta(1 - \xi)] \\ & + [(s + \psi_{in})(Bi - 1) - \psi_p] \sinh[\beta(1 - \xi)] \end{aligned} \quad (\text{B.2e})$$

The over bar in the above expressions indicates the Laplace transform of the involved variable and  $s$  is the Laplace transform parameter. In order to demonstrate the equivalence of Eqs. (B.1) with Eqs. (2.2), in the first stage, the Laplace transform operator is applied to Eqs. (2.2) to obtain

$$\begin{aligned} \bar{U}_p(\xi, s) = & \alpha U_{p0} \int_{\xi_0=0}^{\xi_0=1} \bar{G}_p(\xi, \xi_0, s) \xi_0^2 d\xi_0 + \frac{Bi}{\psi_p} U_{f0} \bar{G}_f(\xi, 1, s) \\ & + Bi \frac{\psi_{in}}{\psi_p} \bar{U}_{in}(s) \bar{G}_f(\xi, 1, s) \\ & - \Phi^2 \int_{\xi_0=0}^{\xi_0=1} \bar{G}_p(\xi, \xi_0, s) \bar{R}_p \xi_0^2 d\xi_0 \end{aligned} \quad (\text{B.3a})$$

$$\begin{aligned} \bar{U}_f(s) = & \alpha U_{p0} \int_{\xi_0=0}^{\xi_0=1} \bar{G}_f(1, \xi_0, s) \xi_0^2 d\xi_0 + Bi U_{f0} \bar{H}^0(1, 1, s) \\ & + \psi_{in} Bi \bar{U}_{in}(s) \bar{H}^0(1, 1, s) \\ & - \Phi^2 \int_{\xi_0=0}^{\xi_0=1} \bar{G}_f(1, \xi_0, s) \bar{R}_p \xi_0^2 d\xi_0 \end{aligned} \quad (\text{B.3b})$$

In the second stage, the boundary value problem that defines the Green's function is solved in the Laplace

domain to obtain

$$\bar{G}_f(\xi, 1, s) = \psi_p \frac{\sinh(\beta \xi)}{\beta M(0, s) \xi} \quad (\text{B.4a})$$

$$\bar{G}_p(\xi, \xi_0, s) = \frac{1}{\beta M(0, s) \xi_0 \xi} \begin{cases} M(\xi_0, s) \sinh(\beta \xi), & \text{for } 0 < \xi < \xi_0 \\ M(\xi, s) \sinh(\beta \xi_0), & \text{for } \xi_0 < \xi < 1 \end{cases} \quad (\text{B.4b})$$

The details to obtain the above expressions are given in Appendix C. In the following stage of the demonstration, the use of Eqs. (B.4) allows showing that the first three terms in the RHS of Eqs. (B.3) are equivalent to the corresponding terms in Eqs. (B.1). Then, the comparison of the terms that contain the reaction rate of Eqs. (B.1b) and (B.3b) confirms that the Green's function given by Eq. (B.4a) for  $\bar{G}_f$  is correct. Finally, comparison of the last terms of Eqs. (B.1a) and (B.3a) leads to an equation for  $\bar{G}_p$  that is identical to Eq. (B.4b). In this way, it is shown that the solutions derived in this section are, without any additional supposition, identical to the ones obtained using Green's functions in Section 2.

## Appendix C Determination of Green's functions in the Laplace domain

In this section we find the Green's functions in the Laplace domain that complete the derivations provided in Appendix B. Application of the Laplace transform to the governing equations for  $G_p(\xi, \xi_0, \tau - \tau_0)$  and  $G_f(\xi, \xi_0, \tau - \tau_0)$  leads to

$$\alpha s \bar{G}_p^0 = \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial \bar{G}_p^0}{\partial \xi} \right) + \delta(\xi - \xi_0) \quad (\text{C.1a})$$

$$s \bar{G}_f^0 = -\psi_{in} \bar{G}_f^0 + \psi_p \left( \bar{G}_p^0 \Big|_{\xi=1} - \bar{G}_f^0 \right) \quad (\text{C.1b})$$

which are coupled by means of the boundary condition

$$\xi = 1, \quad -\frac{\partial \bar{G}_p^0}{\partial \xi} = Bi \left( \bar{G}_p^0 \Big|_{\xi=1} - \bar{G}_f^0 \right) \quad (\text{C.1c})$$

The solution of Eq. (C.1a), for  $\xi \neq \xi_0$ , yields

$$\bar{G}_p^0(\xi, \xi_0, s) = \begin{cases} A \frac{\sinh(\beta \xi)}{\xi}, & \text{for } 0 < \xi < \xi_0 \\ C \frac{\sinh(\beta \xi)}{\xi} + D \frac{\cosh(\beta \xi)}{\xi}, & \text{for } \xi_0 < \xi < 1 \end{cases} \quad (\text{C.2})$$

with  $\beta = \sqrt{\alpha s}$ . Using the boundary condition in Eq. (C.1c), taking into account Eq. (C.1b) to replace  $\bar{G}_f^0$  allows writing Eq. (C.2) as

$$\bar{G}_p^0(\xi, \xi_0, s) = \frac{D}{\xi M(0, s)} \begin{cases} M(\xi_0, s) \frac{\sinh(\beta \xi)}{\sinh(\beta \xi_0)}, & \text{for } 0 < \xi < \xi_0 \\ M(\xi, s), & \text{for } \xi_0 < \xi < 1 \end{cases} \quad (\text{C.3})$$

The additional boundary condition that is needed to close the above expression results from integration of Eq. (C.1a) from  $\xi = \xi_0^-$  to  $\xi = \xi_0^+$ , giving rise to the following flux jump condition

$$\xi_0^2 \frac{\partial \bar{G}_p^0}{\partial \xi} \Big|_{\xi_0^+} - \xi_0^2 \frac{\partial \bar{G}_p^0}{\partial \xi} \Big|_{\xi_0^-} = -1 \quad (\text{C.4})$$

The constant  $D$  can be found by the enforcement of this interfacial boundary condition, the resulting expression for  $\bar{G}_p^0$  is given by

$$\bar{G}_p^0(\xi, \xi_0, s) = \frac{1}{\beta M(0, s) \xi_0 \xi} \begin{cases} M(\xi_0, s) \sinh(\beta \xi), & \text{for } 0 < \xi < \xi_0 \\ M(\xi, s) \sinh(\beta \xi_0), & \text{for } \xi_0 < \xi < 1 \end{cases} \quad (\text{C.5a})$$

Finally, the combination of Eqs. (C.1b) and (C.5a) yields the fluid Green's function in the Laplace domain

$$\bar{G}_f^0(\xi, 1, s) = \psi_p \frac{\sinh(\beta \xi)}{\beta M(0, s) \xi} \quad (\text{C.5b})$$