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# Low to moderate Peclet mass transport in assemblages of spherical particles for a realistic adsorption–reaction–desorption mechanism

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**Abstract**

A theoretical model and the associated numerical simulations for the mass transport from a moving Newtonian fluid to an assemblage of spherical solid absorbers are presented here. In particular, we present results from the numerical solution of the convection–diffusion equation in the simplified sphere-in-cell geometry and in stochastically constructed 3-D spherical particle assemblages for low to moderate Peclet numbers ($\mathrm{Pe} < 100$) and relatively high porosities ($\epsilon > 0.7$). A realistic adsorption/reaction/desorption mechanism is used to describe the adsorption of diluted mass on the particles surface as opposed to the assumption of instantaneous and Langmuir-type adsorption that has been adopted in previous works. We also attempt to compare the effect of considering different sorption mechanisms in terms of adsorption efficiency. In all cases, the adequacy of the simplified sphere-in-cell approach is tested against the predictions from the numerical study in sphere assemblages. It is found that higher adsorption efficiencies correspond to lower porosities while increasing Peclet numbers lead to lower $\lambda_0$ values. Finally, it is shown that the assumption of instantaneous adsorption leads to severe overestimation of the adsorption efficiency in comparison with that obtained by using the more realistic adsorption–reaction–desorption model.

*Keywords:* Granular media; Peclet number; Adsorption; Flow; Mass transfer

## 1. Introduction

The mass transport within assemblages of spherical particles is of great importance in a variety of industrial and technological applications [1,2]. This holds especially in the case of low Reynolds number flow, where analytical solutions can be obtained for the flow field and the mass diffusion and/or adsorption process in simplified geometries [3–5]. On the other hand, significant effort has been put in numerical solutions of the Stokes equations in realistic reconstructions of porous media (including spherical particle assemblies), usually with reference to material transport properties predictions [6,7]. Additionally, several theoretical investigations have been presented for the relevant transport problems concerning either high Peclet values and therefore analytical approaches [8–12], or low ones where numerical simulations are necessary [13–19].

In the aforementioned works the particles were assumed to adsorb mass instantaneously [8,9,12,14]. It is obvious that the approach of instantaneous adsorption pertains to a very limited range of applications, as it is a quite rare physicochemical phenomenon. Recently, a rather detailed model considering also Langmuir-type adsorption for the spherical grains of the assemblage has been presented by Coutelieris et al. [19]. An extended version of this model is adopted here to simulate adsorption – heterogeneous reaction – desorption mechanisms, which can describe the sorption process of the diluted solute upon the solid surface with high accuracy [20–23]. More specifically, it can be considered that the solute diluted in the bulk phase is initially adsorbed by the solid surface where a heterogeneous reaction takes place and its products, which are assumed to be inactive and of very low concentrations, are again desorbed in the bulk phase. The adsorption is assumed to occur due to vacant sites that are normally distributed over the surface area while the whole process is determined by an overall rate according to thermodynamics [24].

In the present work, we compare the semi-analytical approach, based on the analytical solution of the flow-field

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and the subsequent numerical solution of the mass transport problem in the simplified sphere-in-cell geometry, with the numerical simulations for the creeping flow-field in stochastically constructed 3-D sphere assemblages and the subsequent numerical solution of the convection–diffusion problem in this realistic geometry. In all cases, relatively low Peclet values are considered while the selected porosities vary from very large values (close to unity) to intermediate ones. As already mentioned, a realistic adsorption/heterogeneous reaction/desorption mechanism is employed to describe the sorption process on the particle surface as an alternative to the simpler case of instantaneous or Langmuir-type adsorption that have been studied previously [19]. The adsorption efficiency is calculated in all cases and appropriate comparisons are made in that respect too.

## 2. Solution of the flow and mass transfer problem in the sphere-in-cell geometry

The sphere-in-cell geometry has been repeatedly used as a simple model for the representation of the actual complicated geometry of the pore space in spherical particle assemblages and the approximation of the flow-field therein and is graphically presented in Fig. 1. The governing equation for the steady state mass transport in the fluid phase flowing within the model can be written in spherical coordinates as:

$$u_r \frac{\partial c_A}{\partial r} + \frac{u_\theta}{r}\frac{\partial c_A}{\partial \theta} = D\left(\frac{\partial^2 c_A}{\partial r_2} + \frac{2}{r}\frac{\partial c_A}{\partial r} + \frac{1}{r^2}\frac{\partial^2 c_A}{\partial \theta^2} + \frac{\cot\theta}{r^2}\frac{\partial c_A}{\partial \theta}\right) \tag{1}$$

where $c_A$ is the concentration of substance A in the fluid phase, $u_r$ and $u_\theta$ are the $r$-and $\theta$-velocity components, which can be expressed according to Kuwabara's approach [4] as:

$$u_r = -2\left[\frac{F_1}{r^3} + \frac{F_2}{r} + F_3 + F_4 r^2\right]\cos\theta \tag{2a}$$

$$u_\theta = -\left[\frac{F_1}{r^3} - \frac{F_2}{r} - 2F_3 - 4F_4 r^2\right]\sin\theta \tag{2b}$$

where

$$F_1 = -\frac{U_\infty}{4F_5}\left(1 - 2\frac{\alpha^3}{\beta^3}\right) \tag{2c}$$

$$F_2 = -\frac{3U_\infty}{4F_5} \tag{2d}$$

$$F_3 = -\frac{U_\infty}{2F_5}\left(1 + \frac{\alpha^3}{2\beta^3}\right) \tag{2e}$$

$$F_4 = -\frac{3U_\infty}{20F_5}\left(\frac{\beta^3}{\alpha^3}\right) \tag{2f}$$

$$F_5 = \left(1 - \frac{\alpha}{\beta}\right)^3\left(1 + \frac{6\beta}{5\alpha} + \frac{3\beta^2}{5\alpha^2} + \frac{\beta^3}{5\alpha^3}\right) \tag{2g}$$

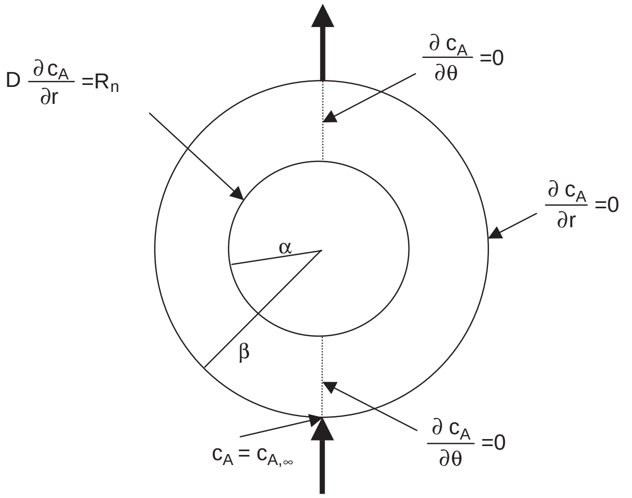

Fig. 1. The sphere-in-cell model.

and $U_\infty$ is the approaching fluid (bulk) velocity far from the solid surface. $D$ in Eq. (1) is the diffusion coefficient of substance A in the solution. The above equation is to be integrated along with the following boundary conditions [19]:

$$c_A(r = \beta,\ \theta = \pi) = c_{A,\infty} \tag{3a}$$

$$\left.\frac{\partial c_A}{\partial_r}\right]_{r=\beta} = 0, \quad 0 \le \theta < \pi \tag{3b}$$

$$\left.\frac{\partial c_A}{\partial \theta}\right]_{\theta=\pi} = 0, \quad \alpha < r \le \beta \tag{3c}$$

$$\left.\frac{\partial c_A}{\partial \theta}\right]_{\theta=0} = 0, \quad \alpha < r \le \beta \tag{3d}$$

and

$$\left.D\frac{\partial c_A}{\partial_r}\right]_{r=\alpha} = R_n, \quad 0 < \theta \le \pi. \tag{3e}$$

The conditions described by Eqs. (3a) and (3b) have been proposed by Coutelieris et al. [14] in order to ensure the continuity of the concentration upon the outer boundary of the cell for any Peclet number. Furthermore, Eqs. (3c) and (3d) express the axial symmetry inherent to the sphere-in-cell geometry. The last boundary condition describes the continuity of the mass fluxes on the solid surface while the overall rate $R_n$ is dependent on the type of sorption process considered. For a typical adsorption/heterogeneous reaction/desorption mechanism for the component A upon the solid surface [20,24], $R_n$ is given as:

$$R_n = k_s c_{AS}^n \tag{4}$$

where $k_s$ is the rate constant of the heterogeneous reaction of order n upon the surface. By considering a three step (adsorption/heterogeneous reaction/desorption) concept of the sorption process involving the theory of active (vacant) sites [20], and by assuming very rapid (instantaneous) desorption for the chemically neutral desorbed product, the equality of