

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 ($Pe < 100$) 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 λ_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.

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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 Coutelieiris 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:

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

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

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

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

where

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

$$F_2 = - \frac{3U_\infty}{4F_5} \quad (2d)$$

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

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

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

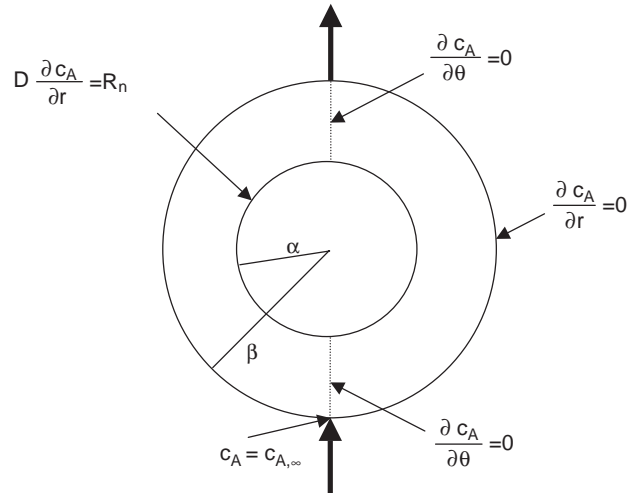


Fig. 1. The sphere-in-cell model.

and U_∞ 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]:

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

$$\left. \frac{\partial c_A}{\partial r} \right]_{r=\beta} = 0, \quad 0 \leq \theta < \pi \quad (3b)$$

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

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

and

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

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:

$$R_n = k_s c_{AS}^n \quad (4)$$

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

the rates per step corresponds to a non-linear equation for the concentration of component A, c_{AS} , upon the solid surface:

$$k_s c_{AS}^n + [k_d + k_a c_A(\alpha, \theta) N] c_{AS} - k_a c_A(\alpha, \theta) \xi_m = 0 \quad (5)$$

where k_a and k_d denote the adsorption and desorption rate constants of component A, respectively, ξ_m is the concentration of the vacant sites of the solid surface and N is Avogadro's number. In physical terms, the first term of the above equation represents the molar flux due to reaction, the second one corresponds to the mass flux approaching the surface while the last one describes the flux due to adsorption. Overall, the above equation correlates the hard-to-measure surface concentration of A, c_{AS} , with its concentration in the bulk phase very close to the solid surface, $c_A(\alpha, \theta)$ by considering the balance for the active sites on the adsorbing surface. In general, only the cases of $n=0$, $n=1$ and $n=2$ are of practical importance but zeroth order reactions are of very limited applications [20]. Therefore, the present investigation deals only with first ($n=1$) and second ($n=2$) order heterogeneous reactions. Finally, it should be stressed that the boundary condition (3e) implies non-linearity in the whole approach and, therefore, an iterative technique is necessary to obtain the numerical solution of Eq. (1).

The adsorption efficiency of a grain in cell, λ_o , is defined by the ratio of the rate with which the solute is sorbed divided by the rate of the upstream influx and can be written as:

$$\lambda_o = \frac{\alpha^2}{4\pi\beta^2} \int_0^\pi \sin\theta \left(\frac{\partial(c_A/c_{A,\infty})}{\partial(r/\alpha)} \right)_{r=\alpha} d\theta. \quad (6)$$

To solve the boundary value problem described above (using the Kuwabara expressions for the velocity components), a non-uniform finite-difference scheme has been employed. For these cases, the value of λ_o can be calculated once the r -component of the concentration gradient upon the surface is known by using a modified Newton–Cotes numerical method with adjustable step for the integration.

3. Solution of the flow and mass transfer problem in spherical particle assemblages

In the previous section, a simplified geometry (sphere-in-cell) is employed to obtain numerical solutions of Eq. (1). Here we consider digitally constructed spherical particle assemblages as a more realistic geometry for the solution of the flow and mass transfer problem. The representation of the biphasic domains under consideration is achieved by the random deposition of spheres of a given radius in a box of specified length. The structure is digitized and the phase function (equal to zero for solid and unity for the pore space) is determined in order to obtain the specified porosity (see Fig. 2 for a sample medium of $\epsilon=0.7243$). The size of the digitized domains is $102 \times 102 \times 102$ and the length of the simulation box is ten times the sphere radius. Details of the efficient algorithm (ballistic deposition) used for the stochastic construction of the porous medium can be found in [19].

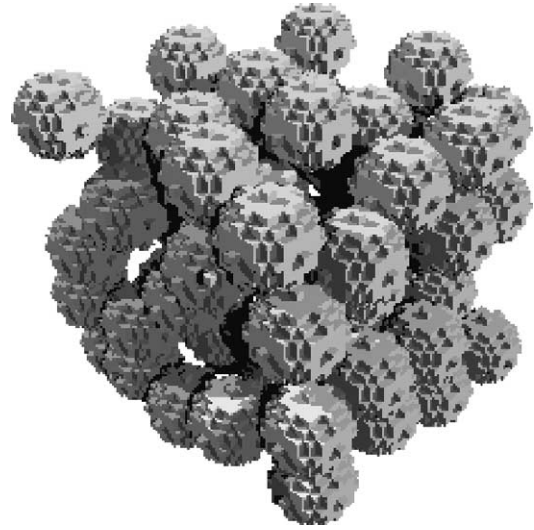


Fig. 2. Stochastically constructed 3-D sphere assemblage for $\epsilon=0.7243$.

To obtain the flow-field within such an assemblage for the creeping flow of a Newtonian incompressible fluid, the Stokes equation (momentum conservation) coupled with the continuity equation (mass conservation) should be integrated along with boundary conditions imposing spatial periodicity and no-slip at the surface of the solid elements of the domain (see [19] for details). The consequent numerical solution is achieved with the use of a finite-difference scheme in conjunction with the artificial compressibility relaxation algorithm [25–27]. The pore space is discretized through a marker-and-cell (MAC) mesh with the pressure defined at the center of the cell, and the velocity components defined along the corresponding face boundaries. The resulting linear system of equations is solved by the successive over-relaxation method.

Following the determination of the velocity field, the time-dependent mass transport of a passive solute in the stochastically constructed medium is described by the convection–diffusion equation:

$$\frac{\partial c_A}{\partial t} + u \cdot \nabla c_A = D \nabla^2 c_A. \quad (7)$$

The adsorption mechanism employed above in the sphere-in-cell model, i.e. Eqs. (3e),(4),(5), is also considered at the fluid-solid interfaces of the reconstructed assemblage. The equations describing the boundary value problem are discretized using finite differences with an upwind numerical scheme where the type (forward or backward) of the discretization of the local first derivatives in any direction is chosen depending on the actual direction of the velocity component in every location in the domain. The resulting linear systems of equations are solved using the SOR technique. Finally, the adsorption efficiency is determined as:

$$\lambda_o = \frac{\iint_{S_{outlet}} c_A u n dS}{\iint_{S_{inlet}} c_A u n dS} \quad (8)$$

4. Results and discussion

The relative agreement between the results produced by considering the sphere-in-cell approximation and those obtained from the numerical solution in the 3-D sphere assemblages is presented in Fig. 3. By assuming a typical value for ξ_m (1 active site per \AA^2), the values of the sorption constants are: $k_a = 1 \times 10^{-30} \text{ m}^3 \text{ s}^{-1}$, $k_d = 8 \times 10^{-3} \text{ s}^{-1}$ and $k_s = 8 \times 10^{-3} \times 100^{(1-n)} (\text{kg m}^{-2})^{1-n} \text{ s}^{-1}$ since the dimension of each term in Eq. (5) is mass per unit area per unit time. These values can be considered as typical [20] and are used in the simulations presented here unless otherwise stated. The figure compares the respective adsorption efficiencies for several porosities ($\epsilon = 0.9883$, $\epsilon = 0.8136$ and $\epsilon = 0.7243$) while the realistic adsorption/reaction/desorption mechanism includes heterogeneous reaction of first (a) and second (b) order. In general, the agreement is almost perfect for all cases when the porosity values are high because the semi-analytical sphere-in-cell model is very close to reality for such high porosity values [19]. As the porosity becomes lower, the semi-analytical approach of the sphere-in-cell model cannot adequately describe the mass transport process for low Pe because the diffusion layer is larger than the cell itself [19]. Despite this, the agreement in Fig. 3 remains quite reasonable for the lower porosities and Pe numbers. Finally, the order of the reaction

does not seem to affect significantly the agreement between the two approaches. It should be noted here that the characteristic length used for the Peclet number in the case of the sphere-in-cell model is the radius of the inner sphere, α . For the case of numerical simulations in sphere packings, the characteristic length is the radius of an “equivalent” sphere having the same volume with the total volume of the spheres actually included in the assemblage.

On the other hand, as Peclet values increase, the transport process becomes more and more convective and the analytical flow-field of the sphere-in-cell is not any more a sufficient approximation of the actual flow-field in real granular media thus leading to discrepancies of the model. The influence of the Peclet number on the adsorption efficiency for $\epsilon = 0.7243$ is presented in Fig. 4. The calculations were done using the full-numerical scheme where the following types of sorption are assumed: instantaneous, Langmuir-type and realistic adsorption/reaction/desorption mechanism with first and second order heterogeneous reaction. The highest efficiency is found for instantaneous adsorption, as the concentration gradients are lower in all the other cases. In general, the assumption of instantaneous adsorption leads to significant overestimation for the adsorption efficiency compared with that obtained by using Langmuir or the more realistic adsorption–reaction–desorption model. In this respect, the instantaneous adsorption could

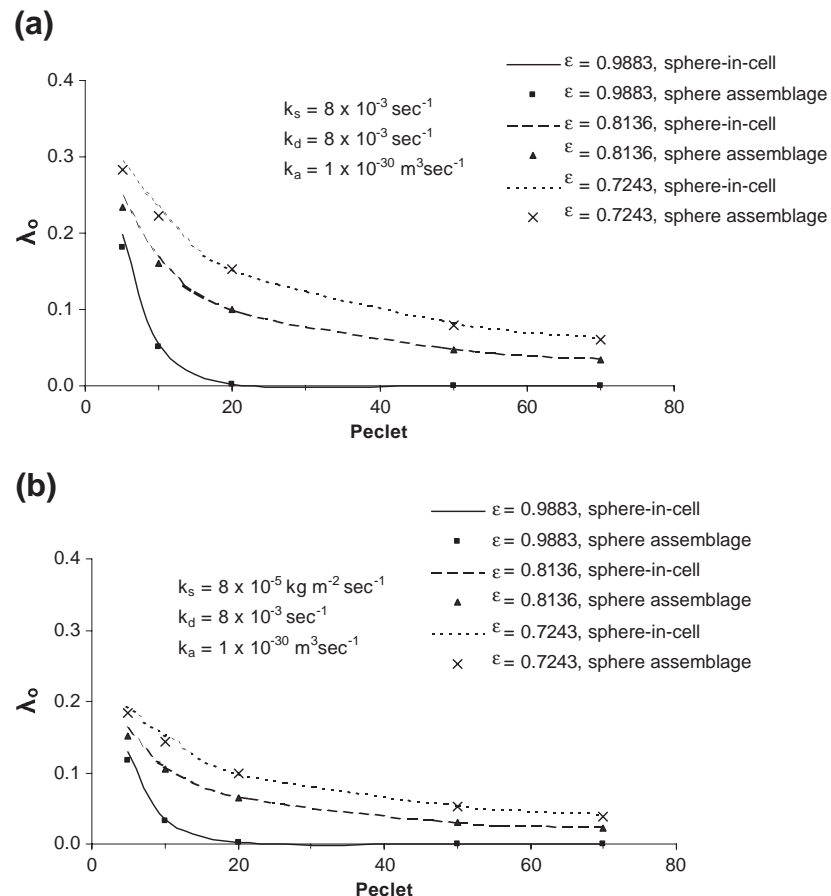


Fig. 3. Comparison between adsorption efficiency in sphere-in-cell and sphere assemblies for different porosities when heterogeneous reaction of first (a) and second (b) order is assumed.

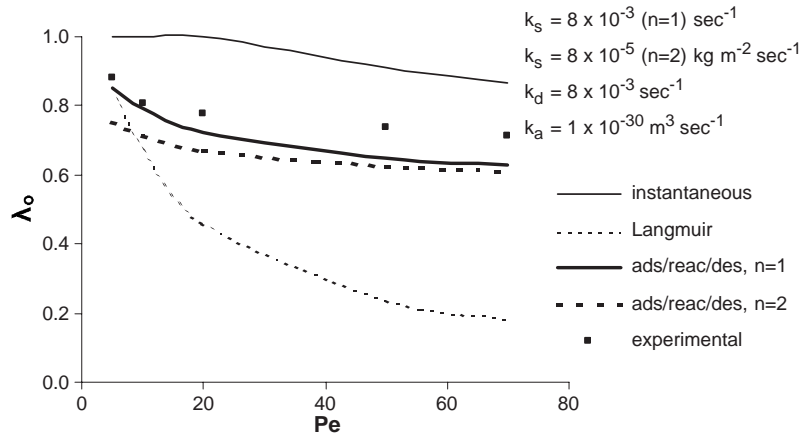


Fig. 4. Adsorption efficiency of the 3-D sphere assemblage as a function of Pe for various adsorption mechanisms: instantaneous, Langmuir-type and ads/reac/des with heterogeneous reaction of first and second order. The discrete points represent experimental data from [28].

be considered as a limiting case (upper limit) of an adsorption/reaction/desorption mechanism ($c_{AS}=0$ in Eq. (5) and $c_A(\alpha,\theta)=0$ set as boundary condition in replacement of Eq. (3e)). A decline of the adsorption efficiency with Pe is also observed because the more convective flows (increasing Peclet) tend to prevent substance A from being captured by the solid surface. The discrete points in the figure represent experimental data of Wilson and Geankoplis [28] that have been appropriately transformed to the present quantities and units [19]. It is important to note that the selected experimental data have been obtained under low Reynolds number to ensure creeping flow conditions. As the actual sorption mechanism in the experiments is not clearly known, the agreement between predictions of the adsorption/reaction/desorption case and the experimental data can be considered as sufficient. This

comparison could be further improved by modifying the adsorption, reaction and desorption rate constants. However, we do not proceed further in this direction, as there is no available experimental information for such rates.

Fig. 5 depicts the relative influence of the reaction, adsorption and desorption rates on the adsorption efficiency. More precisely, Fig. 5a presents λ_o as a function of the ratio of destruction rate of the component A due to reaction divided by the destruction rate of the component A due to adsorption. It is observed that the decrement of the reaction rate (for constant adsorption rate) corresponds to a consequent decrement of the adsorption efficiency because the diluted component has been adsorbed but not destroyed under the same rate and, therefore, remains on the surface filling the vacant sites, i.e. setting barriers in the sorption process of component A. On the other

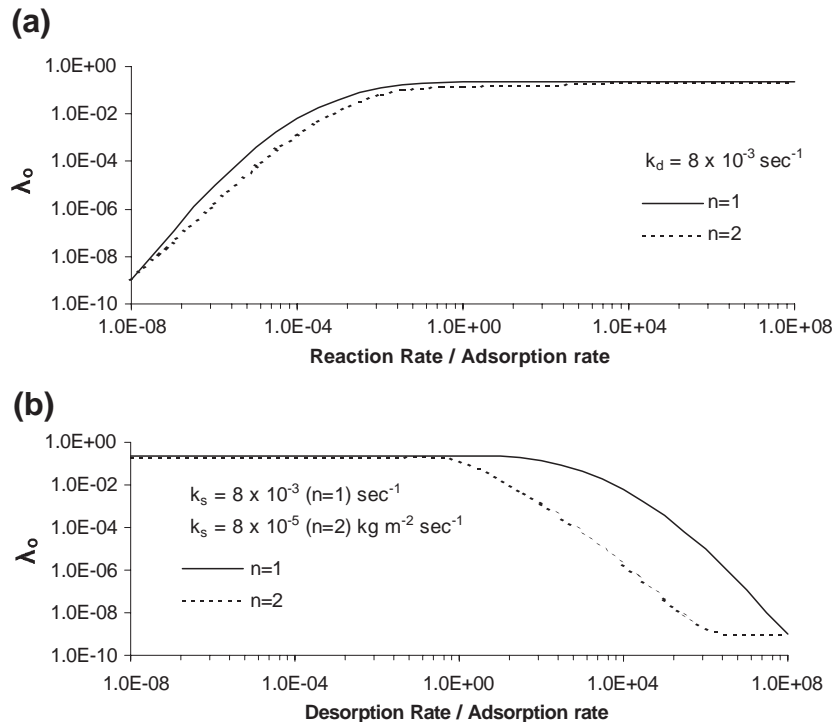


Fig. 5. Dependence of the adsorption efficiency on the ratio of the reaction to the adsorption rates (a) and on the ratio of the desorption to the adsorption rates (b).

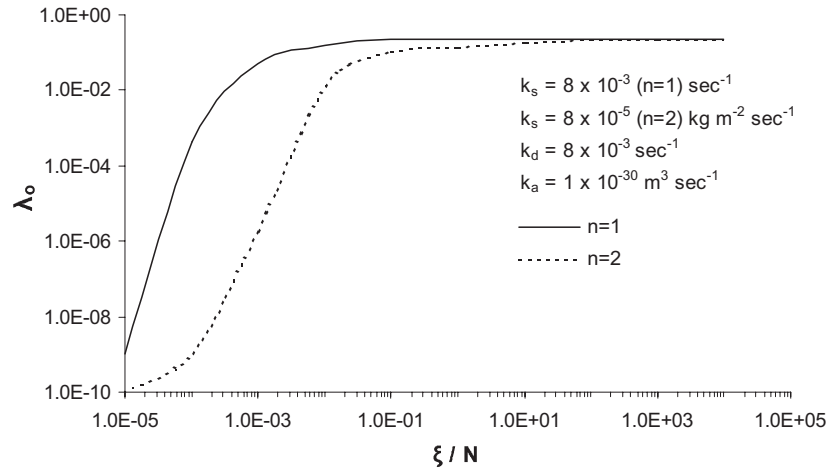


Fig. 6. Dependence of the adsorption efficiency on the normalized surface concentration of vacant sites.

hand, the increment of reaction rate forces the adsorption efficiency to tend asymptotically to a value that is independent on the reaction order. Fig. 5b shows the influence of the ratio desorption/adsorption rate on the overall adsorption efficiency when heterogeneous reactions of first and second order are assumed. It is seen that the increment of the desorption rate beyond a critical value corresponds to a decrease of efficiencies down to very low values. Additionally, the higher the order of the heterogeneous reaction is, the higher the possibility for the component A to escape from the adsorption area. This effect is more clear for the case when the desorption rate is practically dominant.

Fig. 6 presents the dependence of the adsorption efficiency on the normalized concentration of the vacant sites, ξ_m/N . It is observed that lower values of ξ_m/N correspond to very low adsorption efficiencies because there are not enough vacant sites to sufficiently adsorb the diluted mass. This behavior is more pronounced for heterogeneous reactions of higher order. On the other hand, there is a critical value for the normalized concentration of the vacant sites, above which the adsorption efficiency is practically constant (set by the reaction rate).

5. Conclusions

Analytical and numerical investigations for the mass transport from a moving Newtonian fluid to an assemblage of spherical solid absorbers are presented for low to moderate Peclet values ($Pe < 100$) and relatively large porosities ($\varepsilon > 0.7$). In the present work, the sphere-in-cell approach permits the analytical determination of the velocity field, which is then used for the solution of the convection–diffusion equation within the domain defined by the cell. In addition, we attempt a numerical solution of the flow-field and the corresponding convection–diffusion problem in the more realistic geometry of stochastically constructed 3-D sphere assemblages. In all cases, we consider: (a) instantaneous adsorption, (b) Langmuir-type adsorption as well as a realistic sorption mechanism involving first (c) and second (d) order heterogeneous reaction. The adsorption efficiency is calculated as a function of Pe and porosity and the adequacy of the simplified semi-analytical

approach (sphere-in-cell) is tested against the predictions from the numerical study in sphere assemblages. It is found that higher efficiencies correspond to lower porosity while increasing Peclet numbers lead to lower λ_0 values. Moreover, the consideration of instantaneous adsorption yields higher values of the adsorption efficiency at the same Peclet number and porosity than those calculated in any other case. The adsorption/reaction/desorption mechanism provides a reasonable estimation of the adsorption efficiency tendency compared to available experimental measurements.

Nomenclature

c_A	concentration of component A
c_{AS}	concentration of component A on the solid surface
$c_{A\infty}$	concentration of component A far away from the absorbing area
D	diffusion coefficient of the diluted component A in the bulk phase
F_1, F_2, F_3, F_4, F_5	coefficients for the velocity components defined by Eqs. (2c–g)
k_a, k_d, k_s	adsorption, desorption and heterogeneous reaction rate constants, respectively
N	Avogadro's number
n	order of the heterogeneous reaction
Pe	Peclet number ($=U_\infty \alpha / D$)
r	spherical coordinate
R_n	overall adsorption rate
S	surface
S_{inlets}, S_{outlet}	inlet and outlet surface, respectively
t	time
u	fluid velocity vector
U_∞	approaching fluid velocity far from the solid surface
u_r, u_θ	r - and θ -component of the fluid velocity, respectively

Greek Letters

α	radius of the inner sphere in the sphere-in-cell model
β	radius of the outer sphere in the sphere-in-cell model
θ	spherical coordinate
λ_0	overall adsorption efficiency
ξ_m	site concentration (= vacant sites per unit surface)

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