The influence of axial orientation of spheroidal particles on the adsorption rate in a granular porous medium

F. A. Coutelieris

National Center for Scientific Research 'Demokritos', 15310 Aghia Paraskevi Attikis, Greece

The mass transport problem from a Newtonian fluid to a swarm of prolate and/or oblate spheroidal adsorbers under creeping flow conditions is considered here. The spheroidal-in-cell model is used for the analytical description of the flow field within the swarm. The convective diffusion equation along with the appropriate boundary conditions for the description of the adsorption upon the solid surface is solved analytically for high Peclet numbers and numerically in the low Peclet regime. In both cases, analytical expressions for the adsorption rate are obtained. It is found that the oblate geometry offers significant advantage for capturing the diluted mass compared with the prolate one even in strongly convective environments. It is also shown that the assumption of instantaneous adsorption overestimates significantly the adsorption efficiency.

1. INTRODUCTION

Modeling mass transport through swarms of particles has attracted significant interest mainly in relation to fluid flow and the associated physicochemical processes. Most of the proposed models derive analytical solutions for the mass transport problem under creeping flow conditions by assuming spherical or cylindrical shape of the particles [1]. Happel and Kuwabara have presented models that solve analytically the creeping flow problem for spherical geometry [2,3]. Both these models are based on the representation of the overall solid mass of the swarm by just one spherical particle, which is embedded in a spherical or cylindrical liquid envelope keeping the porosity equivalent to that of the swarm. However, in almost all practical applications, the particles are of spheroidal shape instead of spherical [4]. An analytical model for the representation of the flowfield within the swarm of spheroidal particles has recently been proposed for both Happel- and Kuwabara-type boundary conditions [5,6]. This analytical solution has already been applied in the study of mass transport processes within swarms of spheroidal particles for both high and low Peclet values [7,8] in a way quite analogous to previous investigations concerning particles of spherical shape [9-11].

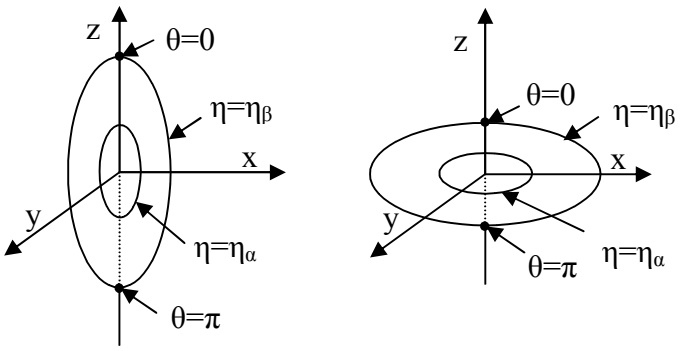

Fig. 1. Prolate and oblate "spheroid-in-cell" models

The weak point of all these approaches is the postulation of instantaneous adsorption occurring on the liquid-solid interface. This approximation, based on the assumption of the very thin diffusion layer, which is valid only for high Peclet values, produced analytical expressions for the concentration profile in that regime, while, for low *Pe* a numerical treatment is necessary. Unfortunately, instantaneous adsorption is rather rare corresponding to a very limited range of applications. A more realistic approach is adopted here based on an adsorption - heterogeneous reaction - desorption mechanism, which describes the adsorption of the diluted mass upon the solid surface with high accuracy [12-15]. More precisely, it can be supposed that the component A, which is diluted in the bulk phase, is initially adsorbed by the solid surface where a heterogeneous reaction takes place and its products, which are considered inactive and of very low concentration, are again desorbed in the bulk phase. The adsorption is assumed to occur due to vacant sites that are normally distributed over the solid surface while the whole process can be described by an overall rate according to basic thermodynamics analysis [16].

2. THEORY

Consider a solid spheroid having long semi-axis a_3 and semi-focal distance $\alpha = \sqrt{a_3^2 - 1}$, which is surrounded by another confocal spheroidal liquid envelope, whose thickness is adjusted so that the porosity of the granular medium is equal to that of the model. The spheroidal-in-cell model, predicts the stream function, Ψ, for creeping flow conditions in the prolate coordinates system (η,θ) as follows [5]:

$$\Psi(\eta,\theta) = \frac{\alpha}{D}\{\Lambda_2 G_2(\cosh\eta) + \Lambda_3 [\frac{5G_4(\cosh\eta_\beta)}{G_1(\cosh\eta_\beta)} G_1(\cosh\eta) + G_4(\cosh\eta)] + \Lambda_4 H_2(\cosh\eta)\} G_2(\cos\theta) \quad (1)$$

where D, Λ_2, Λ_3 and Λ_4 are η- and θ-dependent coefficients defined in Dassios et al. [5] and $G_n(x)$ and $H_n(x)$ are the Gegenbauer polynomials of the first and second kind, respectively, of degree –1/2 and of order n.

The governing equation for the steady state mass transport in the fluid phase within the porous medium can be written in prolate spheroidal coordinates and in dimensionless form as:

$$u_\eta \frac{\partial c_A}{\partial \eta} + u_\theta \frac{\partial c_A}{\partial \theta} = \frac{Pe^{-1}}{\alpha\sqrt{\sinh^2\eta + \sin^2\theta}} (\frac{\partial^2 c_A}{\partial \eta^2} + \coth\eta \frac{\partial c_A}{\partial \eta} + \frac{\partial^2 c_A}{\partial \theta^2} + \cot\theta \frac{\partial c_A}{\partial \theta}) \quad (2)$$

The above equation can be integrated with the following boundary conditions:

$$c_A(\eta=\eta_\beta,\theta)=1, \qquad 0 \le \theta \le \pi \tag{3a}$$

$$\left.\frac{\partial c_A}{\partial \eta}\right]_{\eta=\eta_\beta} = 0, \qquad 0 \le \theta < \pi \tag{3b}$$

$$\left.\frac{\partial c_A}{\partial \theta}\right]_{\theta=\pi} = 0, \qquad \eta_\alpha \le \eta \le \eta_\beta \tag{3c}$$

$$\left.\frac{\partial c_A}{\partial \theta}\right]_{\theta=0} = 0, \qquad \eta_\alpha \le \eta \le \eta_\beta \tag{3d}$$

and

$$\frac{Pe^{-1}}{\alpha\sqrt{\sinh^2\eta_\alpha + \sin^2\theta}}\left[\frac{\partial c_A}{\partial \eta}\right]_{\eta=\eta_\alpha} = k_s c_{AS}, \qquad 0 < \theta < \pi \tag{3e}$$

The first boundary condition is equivalent to the well-known Levich approach (c_A=1 for $\eta \to \infty$), according to which, it is supposed that the concentration values vary only within a very thin concentration layer while it is supposed to keep its bulk value elsewhere [9]. Eq. (3b) has been proposed by Coutelieris et al. [8] in order to ensure the continuity of the concentration upon the outer boundary of the cell for any Peclet number. Furthermore, eq. (3c) and (3d) express the axial symmetry that has been assumed for the problem. The boundary condition (3e) can be considered as a significant improvement of Levich approach, where instantaneous adsorption on the solid-fluid interface ($c_A(\eta=\eta_\alpha,\theta)$=0) is also assumed for any angular position θ. In particular, eq. (3e) describes a typical adsorption, 1st order reaction and desorption mechanism for the component A upon the solid surface [12,16] where k_s is the rate of the heterogeneous reaction upon the surface and the concentration of component A upon the solid surface, c_{AS}, is calculated by solving the non linear equation

$$\left[k_s + k_A^d + k_A^a c_A(\eta_\alpha,\theta)N\right]c_{AS} - k_A^a c_A(\eta_\alpha,\theta)\xi_m = 0 \tag{4}$$

which relates the surface concentration of A, c_{AS} (a quantity that is difficult to determine experimentally), with its concentration in the bulk phase very close to the solid surface, $c_A(\eta_\alpha,\theta)$. In the above eq. (4), the terms k_A^a and k_A^d denote the adsorption and desorption rate of component A, respectively, ξ_m is the concentration of the vacant sites on the solid surface and N is the Avogadro number [12].

In the high Peclet number regime (Pe >>1), the concentration boundary layer is very thin compared to the local radius of curvature of the particle, and the curvature term $\coth\eta\,\partial c_A/\partial\eta$ can be neglected. The same holds for the tangential diffusion terms $\partial^2 c_A/\partial\theta^2$ and $\cot\theta\,\partial c_A/\partial\theta$, which were also shown to be insignificant for high Peclet values [8]. In this case, eq. (2) becomes parabolic on θ and it can be solved analytically in a manner quite similar to that of Coutelieris et al. [7], providing concentration profiles in the fluid phase as follows

$$c_A(z) = c_2\int_0^z e^{-\frac{4}{9}t^3}\,dt + c_3 \tag{5}$$

where

$$z = \sqrt[3]{\frac{\alpha \, \mathrm{E} \, Pe}{4 \, D \, (\sinh^2 \eta_\alpha \, \text{-}1)}} \; \eta f(\theta) \tag{6}$$

and c_2 and c_3 are coefficients that can be calculated by solving the non-linear system

$$\sqrt[3]{\frac{E}{4\alpha^5 Pe^2}} \frac{f(\theta)}{\sqrt{\sinh^2 \eta_\alpha + \sin^2 \theta}} c_2 \text{ - } R(c_3) = 0 \tag{7a}$$

$$1.17c_2+c_3=1 \tag{7b}$$

where E and $f(\theta)$ are terms defined by Coutelieris et al. [7]. Further mathematical manipulations lead to the following expression for the overall adsorption efficiency, λ_o,

$$\lambda_o = \frac{1.26}{\alpha^2 \sinh^2 \eta_\beta} \sqrt[3]{\frac{E}{Pe}} \int_0^{2\pi} c_2 f(\theta) d\theta \tag{8}$$

which expresses the ratio of the adsorbed mass to the overall amount of mass moving within the porous material.

The corresponding expressions for the case of oblate spheroids-in-cell are quite analogous to those of the prolate case. Differences are observed only in the following equations

$$\sqrt[3]{\frac{E}{4\alpha^5 Pe^2}} \frac{f(\theta)}{\sqrt{\cosh^2 \eta_\alpha \text{ - } \sin^2 \theta}} c_2 \text{ - } R(c_3) = 0 \tag{7a'}$$

and

$$\lambda_o = \frac{1.26}{\alpha^2 \cosh^2 \eta_\beta} \sqrt[3]{\frac{E}{Pe}} \int_0^{2\pi} c_2 f(\theta) d\theta \tag{8'}$$

The moderate and low Peclet regimes are characterized by significant magnitudes of all the terms of eq. (2), which should therefore be solved numerically. A non-uniform finite - difference discretization scheme has been chosen for the system, estimating the overall adsorption efficiency, λ_o, as follows:

$$\lambda_o = \frac{-2\alpha \sinh \eta_\alpha}{Pe \; \alpha^2 \sinh^2 \eta_\beta} \int_0^{\pi} \sin\theta \left(\frac{\partial c_A}{\partial \eta} \right)_{\eta=\eta_\alpha} d\theta \tag{9}$$

and

$$\lambda_o = \frac{2\alpha \sinh \eta_\alpha}{Pe \; \alpha^2 \cosh^2 \eta_\beta} \int_0^{\pi} \sin\theta \left(\frac{\partial c_A}{\partial \eta} \right)_{\eta=\eta_\alpha} d\theta \tag{9'}$$

for the cases of prolate and oblate spheroids, respectively.

3. RESULTS & DISCUSSION

Fig. 2 shows the concentration profiles for the component A at different angular positions for the cases of prolate (a) and oblate (b) spheroids-in-cell. For high Peclet numbers (*Pe*=1000), higher concentration gradients are found for prolate spheroids compared to those for oblate ones, as it has also been observed previously for the case of instantaneous adsorption [7]. Principally, the concentration decreases, as the angular position is closer to the stagnation point and approaches its bulk value at distances less than 25% of the envelope thickness, i.e. close enough to the solid surface in all cases. Dashed lines in Fig. 1 denote the concentration profiles for a low *Pe* value (*Pe*=15). Note that this value has been selected to be high enough to ensure the satisfaction of the condition $\partial c_A / \partial \eta = 0$ at $\eta=\eta_\beta$ and $\theta=0$ [8]. A large reduction of the concentration gradients towards the solid surface is observed, compared with the case of high Peclet numbers, because the diffusion starts playing a dominant role over convection as *Pe* decreases. Furthermore, an important weakness of Levich approach can be observed in the very low concentration regime at $\eta=\eta_\beta$ within the tail region ($\theta \rightarrow \pi$) where the concentration tends to reach the constant bulk value. Levich's approach fails to predict acceptable concentration values in this area because the fundamental assumption of very thin concentration boundary

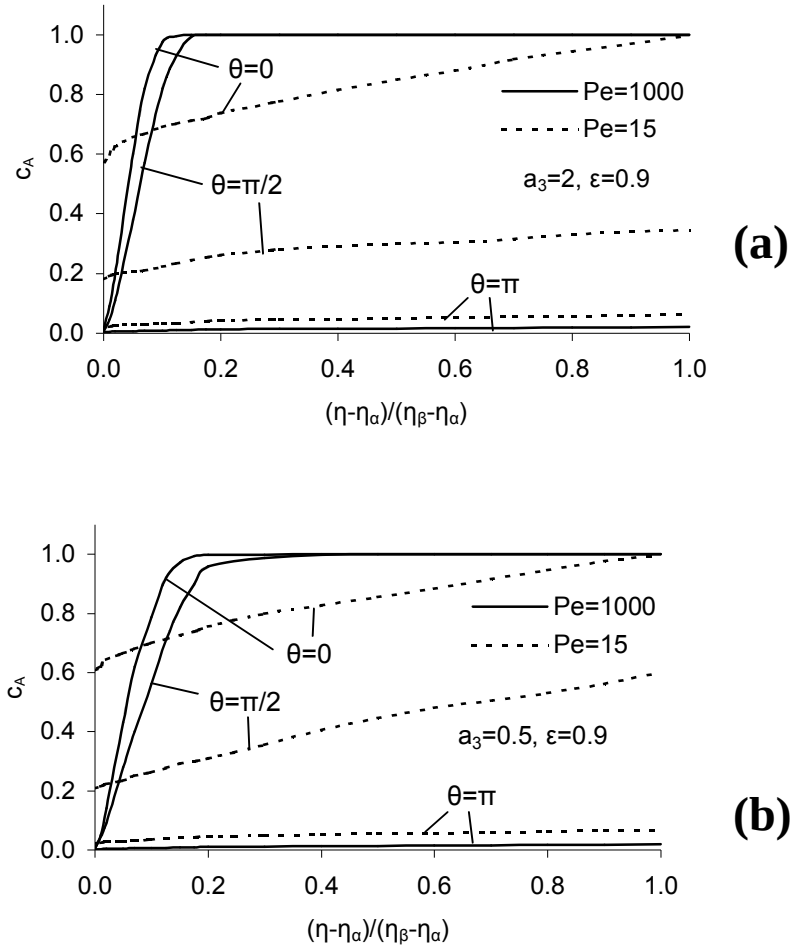

Fig. 2. Concentration profiles for prolate (a) and oblate (b) spheroidal geometry for high and low Peclet at three different angular positions

layer is not valid in this region even for high *Pe*. Finally, it should be stressed that the concentration upon the surface, $c_A(\eta_\alpha,\theta)$, takes its higher value at the impact point and decreases monotonically as θ tends to π for the case of prolate spheroids and high Peclet number. The maximum concentration value appears at the equator for the case of oblate spheroids where the thickness of the diffusion film becomes minimum [8]. This behavior is not observed for low Peclet numbers where the surface concentrations are extremely higher than those of the high *Pe* case and therefore, it can be considered that the accessibility of the solid surface is high enough to produce smooth concentration profiles for the adsorbed mass.
The dependence of the overall adsorption efficiency on the Peclet number for both prolate and oblate geometries is presented in Fig. 2. A considerable decrease of the adsorption efficiency is observed as *Pe* increases. This is expected, as the more convective flows do not allow the component A to be captured by the solid surface. In general, oblate spheroids present higher frontal surface than the prolate ones, and therefore, their ability for adsorption is higher. This advantage of oblate geometry disappears in the case of low Peclet where almost all parts of the adsorbing solid surface become active as the environment becomes more diffusive. The values for the overall adsorption efficiency predicted considering the model of instantaneous adsorption are 10-35% higher, depending on the *Pe*, the geometry, the porosity and the order of the reaction, than those calculated by suggesting the more realistic model of adsorption, described by eq. (3e) & (4) and low Peclet values, because the concentration on the solid surface attains in the latter case non zero values making the difference $c_A(\eta_\beta,\theta)$-$c_A(\eta_\alpha,\theta)$ very small for some θ-values. The impact of this effect is higher than that of the decrease of the concentration gradients observed when the realistic adsorption process is adopted instead of the instantaneous adsorption postulation.

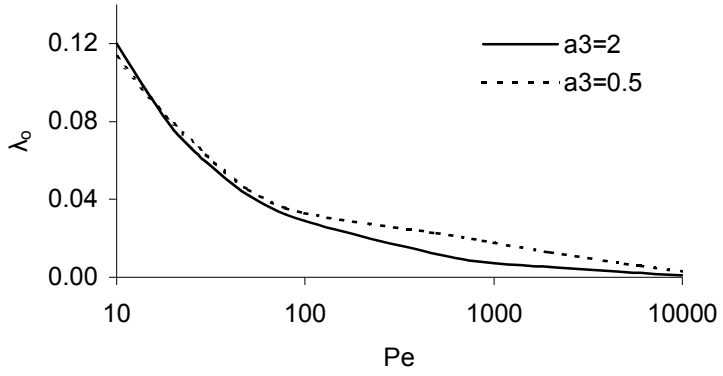

Figure 3: Influence of the Peclet number on the adsorption efficiency for typical prolate and oblate spheroids-in-cell.

4. CONCLUSIONS

The problem of mass transfer from a moving Newtonian fluid to a swarm of prolate and/or oblate stationary spheroidal adsorbing particles under creeping flow conditions is solved using a spheroidal-in-cell model. The flow field through the swarm was obtained by using the spheroid-in-cell model proposed by Dassios et al. [5]. An adsorption – 1st order reaction - desorption scheme is used as boundary condition upon the surface of the spheroid in order to describe the interaction between the diluted mass in the bulk phase and the solid surface. The convective diffusion equation is solved analytically for the case of high Peclet numbers where the adsorption rate is also obtained analytically. For the case of low *Pe* a non-

uniform finite difference scheme is used to treat the problem numerically. It is found that the adsorption rate is higher for oblate spheroids-in-cell compared to spheres-in-cell and prolate spheroids-in-cell. Consequently, the oblate geometry offers a significant advantage compared with the prolate one for convective environments. However, this tendency fades away as the environment becomes diffusive. Results presented here are more accurate than previous ones produced under the assumption of instantaneous adsorption, which leads to a 10-35% overestimation of the adsorption efficiency.

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