The effect of the porosity on the adsorption rate in granular porous media

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The Sherwood number representing the mass transfer coefficient for transport from a moving fluid to a swarm of spherical particles is calculated in the range of high porosities. The mass transport problem is solved both analytically and numerically under the assumption of instantaneous adsorption upon the liquid-solid interface. The velocity components within the liquid phase are obtained either by using the analytical formulations of the sphere-in-cell model or by solving numerically the creeping flow problem in a stochastically constructed packing of spheres. It is found that the agreement between numerical and analytical data is in general reasonably good for the porosity range considered. Limitations of both the numerical and analytical approaches are identified. Numerical predictions are deteriorating rapidly for extremely high porosities (above 0.95). On the other hand, the accuracy of analytically obtained Sherwood values becomes weaker as the porosity decreases because the fundamental assumptions of the analytical model are not satisfied in this case.

Keywords: Peclet number, convection, diffusion, Sherwood number, porosity, granular media

1. INTRODUCTION

Mass transport within high porosity granular porous media is a physicochemical process, which attracts considerable interest from both the research and technological point of view. As porous media are generally characterized by highly complex internal geometry, appropriate modeling of such a process is necessary for the derivation of meaningful conclusions. Several analytical and numerical models have been proposed in this respect, dealing in general with the estimation of the overall mass transport characteristic parameters such as the Sherwood number and the adsorption rate for a wide range of different geometries [1-4]. Most of these models derive analytical solutions for the mass transport problem under creeping flow conditions based on the representation of the overall solid mass of the granular medium by just one spherical particle, which is embedded in a spherical liquid envelope [5,6]. The ratio of the solid volume to the total volume represents the solid volume fraction, i.e. the porosity of the medium. On the other hand, considerable effort has been invested in performing numerical simulations for the study of convection, dispersion and interfacial transport in homogeneous porous media. The macroscopic approach developed by Quintard and Whitaker [7] based on the volume averaging method, is a representative example where efficient numerical schemes for the solution of the local closure problems were also proposed.

In almost all the above models it is supposed that the solid surfaces instantaneously adsorb the mass, which is diluted within the fluid that flows through the medium. This approach has been initially proposed by Levich [8] who obtained analytical expression for the overall Sherwood number for the case of a single isolated sphere in an unbounded fluid. Significant improvements to this model, including the sphere-in-cell model and an intelligent representation of the mass transport conditions, have been presented later [9-11].

The objective of this work is to determine the influence of the Peclet number (expressing the relative importance of convection and diffusion in the medium) on the fluid/solid mass transfer coefficient, expressed by the Sherwood number. The focus in this part of the work is on granular media of relatively high porosities (0.6 to 0.95). To attain this objective, mathematical models for the mass transport problem through a high porosity granular medium under creeping flow conditions are employed. Two approaches are considered: a numerical solution for moderate Peclet values (500□*Pe*□70) and relatively low porosities (ε□0.6) and an analytical approach based on the sphere-in-cell model for high porosities (ε□0.8) and high Peclet values (*Pe*□100). The overall Sherwood number is calculated in all cases and comparisons between analytical and numerical results are performed.

2. MODELING APPROACH

Consider a Newtonian incompressible fluid containing a component A in high dilution (<0.05M) and moving under creeping flow conditions within a relatively high porosity porous medium. The solid surface adsorbs instantaneously the component A. The mass transport regime (convection and/or diffusion) is expressed by the value of the Peclet number, defined as

$$Pe = \frac{\alpha\, u_0}{D} \tag{1}$$

where α is the characteristic length, u_0 is the characteristic velocity and D is the diffusion coefficient.

2.1. Analytical solution

Consider a solid sphere of radius α, which is surrounded by another concentric spherical liquid envelope of radius β, whose thickness is adjusted so that the porosity of the medium is equal to that of the model. The governing equation for the steady state mass transport in the fluid phase within the porous medium can be written in spherical coordinates as

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

where the velocity components are given as [5,6]

$$u_r = \text{-}U\left[1\text{-}\frac{3}{2}\left(\frac{\alpha}{r}\right)+\frac{1}{2}\left(\frac{\alpha}{r}\right)^3\right]\cos\theta \tag{3a}$$

$$u_\theta = U\left[1\text{-}\frac{3}{4}\left(\frac{\alpha}{r}\right)-\frac{1}{4}\left(\frac{\alpha}{r}\right)^3\right]\sin\theta \tag{3b}$$

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

$$c_A\,(r=\beta,\theta)=1, \qquad 0\le\theta\le\pi \tag{4a}$$

$$\left.\frac{\partial c_A}{\partial r}\right]_{r=\beta}=0, \qquad 0\le\theta<\pi \tag{4b}$$

$$\left.\frac{\partial c_A}{\partial \theta}\right]_{\theta=\pi}=0, \qquad \alpha\le r\le\beta \tag{4c}$$

$$\left.\frac{\partial c_A}{\partial \theta}\right]_{\theta=0}=0, \qquad \alpha\le r\le\beta \tag{4d}$$

and

$$c_A\,(r=\alpha,\theta)=0, \qquad 0\le\theta\le\pi \tag{4e}$$

The first boundary condition is equivalent to the Levich approach, given elsewhere as $c_A=1$ for $r\to\infty$ [8]. Eq. (4b) has been proposed by Coutelieris et al. [1] to ensure continuity of concentration at the outer boundary of the cell for any Peclet number. Moreover, eq. (4c) and (4d) represent the axial symmetry assumption considered for this problem. The last boundary condition describes a typical instantaneous adsorption mechanism for the component A upon the solid surface.

For the case of high Peclet numbers (Pe >>1), the concentration boundary layer is very thin compared to the local radius of curvature of the particle, and, thus, the curvature term as well as the tangential diffusion terms can be neglected as it has already been shown [1,8,11]. In that case, eq. (2) becomes parabolic on θ and can be solved analytically in a manner quite similar to that of Levich, providing concentration profiles in the fluid phase of the form

$$c_A(z) \;=\; 1.17\int_0^z e^{-\frac{4}{9}t^3}\,dt \tag{5}$$

where

$$z \;=\; \sqrt[3]{\frac{3\,Pe}{4\alpha^3}}\;r\;\frac{\sin\theta}{\theta\,\text{-}\,0.5\sin2\theta} \tag{6}$$

The overall Sherwood number, $\mathrm{Sh_o}$, is defined as:

$$Sh_o=\frac{\alpha\,k_0}{D} \tag{7}$$

where k_0 is the overall mass transport coefficient. After some mathematical manipulations, the following expression for Sh_o, can be derived

$$Sh_o=\;0.79\sqrt[3]{Pe}\;\int_0^{2\pi} f(\theta)d\theta \tag{8}$$

The moderate and low Peclet numbers correspond to cases where all terms of eq. (2) are significant and numerical solution is required. A non-uniform finite-difference discretization schema has been chosen for solving the boundary value problem of eq. (1) with boundary conditions (3a-e), estimating the overall Sherwood number, Sh_o, as follows:

$$Sh_o = \frac{1}{4\pi a^2} \int_{\pi}^{0} \frac{\left(\partial c_A / \partial r \right)_{r=a}}{c_A(\beta,\theta) - c_A(\alpha,\theta)} d\theta \tag{9}$$

Finally, a predictive form for the overall Sherwood number can be used providing satisfactory predictions for any Peclet value [12]:

$$Sh_o = Sh_o(a, Pe \to 0) + 0.997 g(a) Pe^{1/3} \tag{10}$$

where numerically derived values of $g(a)$ have been tabulated by Coutelieris et al. [13] and respective values for $Sh_o(a, Pe \to 0)$ by Burganos et al. [12].

2.2. Numerical solution

The pore scale boundary value problem is described by the advection-diffusion equation

$$\frac{\partial c_A}{\partial t} + \nabla \cdot \left(\mathbf{v} c_A \right) = D \nabla^2 c_A \tag{11}$$

where c_A is the concentration of component A in the flowing phase, t is time and $\mathbf{v}$ is the interstitial fluid velocity. At the fluid-solid interface it can be considered

$$c_A = 0 \tag{12}$$

To obtain numerically the mass transfer coefficient, a porous medium is stochastically constructed in the form of a sphere pack. Specifically, the representation of the biphasic domains under consideration is achieved by the random deposition of spheres of radius R in a box of length L. 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 porosity and to solve numerically the convection- diffusion problem. The next for this purpose is to obtain the detailed flow field in the porous domain through the solution of the Stokes equations:

$$\nabla p = \mu \nabla^2 \mathbf{v} \tag{13a}$$

$$\nabla \cdot \mathbf{v} = 0 \tag{13b}$$

$$\mathbf{v} = \mathbf{0} \qquad \text{at fluid- solid interface} \tag{13c}$$

where p and μ are the pressure and the viscosity of the fluid, respectively.

A staggered marker-and-cell (MAC) cell is used for the solution of the 3D stokes flow problem in a box made of cubic elements. An initial guess for p is determined through the solution of a Laplace equation. Next, $\mathbf{v}$ is calculated from the corresponding momentum balances and the continuity term $\nabla \cdot \mathbf{v} = 0$ is determined. The pressure is corrected through an artificial compressibility equation of the form:

$$\frac{dp}{dt} = \nabla \cdot \mathbf{v} \tag{14}$$

The above steps are repeated until convergence is reached.

Having determined the velocity field in the medium, the procedure outlined by Quintard and Whitaker [7] is followed to determine through an upscaling procedure the mass transfer coefficient. This approach proceeds by decomposing the local concentration into its interstitial average and a fluctuation

$$c_w = \langle c_A \rangle^w + c'_A = -s_W \langle c_A \rangle^w \tag{15}$$

where the symbol $\langle\ \rangle^w$ represents volume averaging in the fluid phase. The variable s_W is the solution of the equation [7]:

$$D\nabla^2 s_w - \mathbf{v} \cdot \nabla s_w - \varepsilon^{-1} k^* = 0 \tag{16}$$

where $s_w = 1$ at fluid- solid interface, s_W is spatially periodic, $\langle s_w \rangle^w = 0$, and k^* is the mass transfer coefficient defined as:

$$k^* = \frac{1}{V} \int_{A_{ws}} \mathbf{n}_{ws} \cdot \nabla s_w dA \tag{17}$$

By $\mathbf{n}_{WS}$ is denoted the unit vector normal to the fluid-solid interface pointing from fluid to solid while A_{WS} reperesents the area between the fluid-solid phases.

By adopting the decomposition

$$s_w = 1 + k^* \psi \tag{18}$$

where ψ is chosen to be solution of the following boundary value problem:

$$D\nabla^2 \psi - \mathbf{v} \cdot \nabla \psi - \varepsilon^{-1} = 0 \tag{19a}$$

$$\psi = 0 \quad \text{at } A_{ws} \tag{19b}$$

$$\psi \qquad \text{is spatially periodic} \tag{19c}$$

the mass transfer coefficient is given by

$$k^* = -\frac{\varepsilon}{\langle \psi \rangle} \tag{20}$$

because the average of s_W over the porous medium is nullified. The Sherwood number is then determined as:

$$Sh_0 = \frac{k^* l_c}{D A_{ws}} V \tag{21}$$

where l_c is a characteristic length.

The equations (15a-c) are discretized with upwind finite differences and the resulting linear systems of equations are solved using the Succesive Over Relaxation (SOR) technique.

3. RESULTS & DISCUSSION

Fig. 1 presents the overall Sherwood number derived either analytically (continuous line) or numerically (discrete points) as a function of the Peclet number for a relatively high porosity value (ε=0.9). The Sh_o presented here has been unified by simple manipulations to be consistent for both the analytical and numerical approach. An almost monotonic increment of Sh_o is observed as the Peclet values increase because of the higher concentration gradients close to the adsorbing surfaces for highly convective regimes. The agreement between analytical and numerical solutions is very good with a relative difference less than 10% for any Pe value. This kind of agreement can be attributed to the high porosity value used, taking into account that the analytical approach has been shown to be highly accurate in that range [1,11,12]. This is valid the basic assumption made in all such analytical models for an adequate representation of both the velocity components and the concentration profile is that

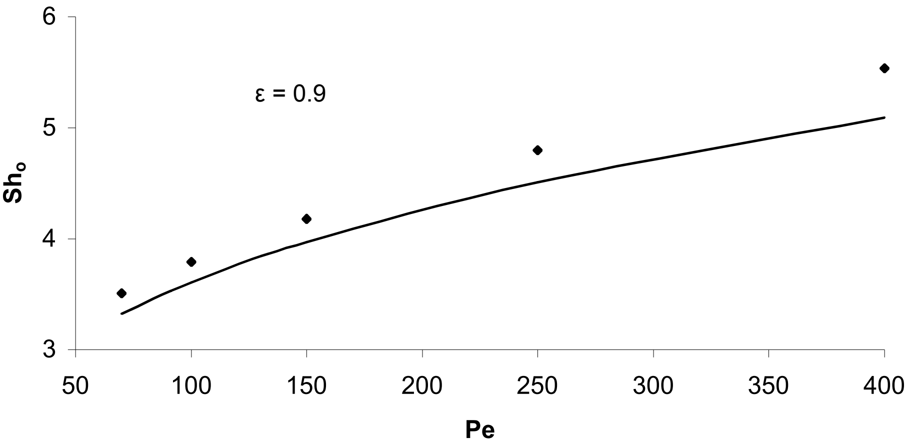

Fig. 1. Dependence of the overall Sherwood number on the Peclet for a high porosity value

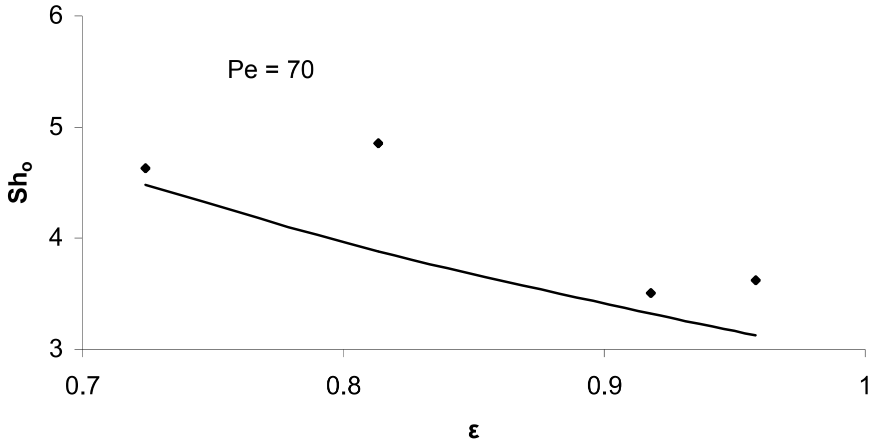

Fig. 2. Influence of the porosity on the overall Sherwood number derived both analytically (compact line) and numerically (discrete points)

of a very thin boundary layer, which corresponds to an outer sphere of radius that is significantly higher than that of the inner one, i.e. the porosity takes quite high values.

The dependence of the overall Sherwood number on the porosity is shown in Fig. 2 for a rather low Peclet value. Evidently, increasing porosities do not favor mass exchange efficiency and the Sh_o drops. High porosity values correspond to low available surface for mass transfer leading to low adsorption rates for the porous material. Numerical predictions are generally in reasonable agreement with the analytical results despite the most "erratic" behavior of the former. This is due to the fact that the high porosities, where the analytical models are in principle applicable, correspond to a very low number of spheres for the numerical representation of the porous medium. Obtaining solutions on an ensemble of stochastically constructed sphere packs may improve the accuracy of the numerical data. On the other hand, it must be pointed out that at porosities lower than 0.8, the available analytical approaches become gradually less accurate and therefore less dependable.

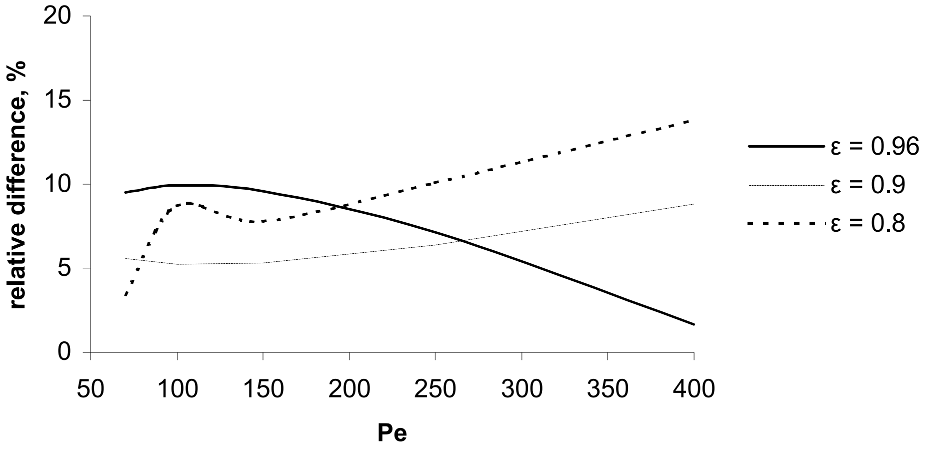

Fig. 3. Relative difference of the analytical to the numerical results for various porosities

This behavior is further exemplified in Fig. 3, where the relative difference of the analytical to the numerical results is presented as a function of the Peclet number for various porosity values. The general agreement can be considered as good enough for any practical use independent of *Pe*.

4. CONCLUSIONS

The problem of mass transfer from a moving Newtonian fluid to a high porosity granular medium considered in this work is characterized by the presence of instantaneously adsorbing spherical particles under creeping flow conditions. Analytical and numerical solutions are derived and compared for high porosities and various Peclet numbers. The well known sphere-in-cell model has been used for the analytical calculation of the flow field while the convection-diffusion equation is solved analytically in accordance to the Levich approach [8] and the associated improvements [1,12,13]. A stochastically constructed sphere pack is considered for the numerical solution of the problem. It is found that the overall Sherwood number is higher as the porosity and Peclet number increase. The comparison of the analytical and numerical approaches shows that both of them are sufficient in different ranges of parameter values (Pe & ε). Indeed, the analytical model is valid for porosities higher than 0.8 while the numerical simulation fails for very high porosity values (ε>0.95).

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