On a homogeneous adsorption in porous materials

Krzysztof Wilmański

(Weierstrass Institute for Applied Analysis and Stochastics, Berlin)

Preprint No. 475

1999

Summary

The paper contains a proposition of a model of adsorption in porous, and granular materials. It is assumed that the mass source resulting from adsorption consists of two contributions: an equilibrium phase change described by the Langmuir isotherm, and a nonequilibrium change due to the relaxation of porosity. The model is illustrated by a simple numerical example of a homogeneous adsorption process.

1. Introduction

Processes of mass exchange between components of mixtures of fluids, and solids belong in most real cases to one of the three fundamental classes: phase changes, chemical reactions or adsorption/desorption processes. Within the first two classes the exchange of mass is accompanied by thermal effects due to the presence of a latent heat of reaction. The processes of the last class can be considered to be isothermal, for instance for a small concentration of adsorbate.

In this work we limit our attention to adsorption processes and consider a construction of the mass source contribution to mass balance equations of a multicomponent continuous model of porous materials. As the basis for this construction we use the model presented in my earlier papers [1,2]. In order to expose clearly the most important intrinsic properties of such sources we investigate a simple example of a homogeneous process. The important coupling of adsorption with diffusion shall be presented in the other two forthcoming papers [3,4].

The model of such a mass exchange between a fluid component, and a solid in porous, and granular materials is based on the classical work of Langmuir [5,6,7] (see also: [8,9] for the discussion of other models). In the original works of Langmuir the theory of adsorption was limited to flat solid surfaces interacting with a gas. On the microscopic level of description of porous, and granular materials we rely on the assumption that particles of the adsorbate change their kinematics from fluid to solid due to a weak van der Waals interaction with internal surfaces of the skeleton (a solid component of the system). The transfer of particles from the fluid component to the internal surface of the solid depends on an area of this surface, and on the number of available *bare sides* on this surface. Their physical interpretation depends on the nature of adsorption processes on internal surfaces, and it shall be discussed in the paper [4]. On the macroscopic level (i.e. in the *representative volume element (REV)* of a porous or granular material) the normalized fraction of these sides per unit volume is denoted by $1-x$, i.e. x is the fraction of *occupied sides*. If the area of the internal surface contained in the representative volume element is denoted by f_{int}, and the mass of adsorbate per unit area of the internal surface by m^A then the amount of mass which can be adsorbed in the representative volume element is equal to the product $m^A f_{int}\,(1-x)$.

Let us denote by V the volume of the representative volume element. Then the amount of mass of adsorbate transfered in unit time from the liquid phase to the solid skeleton is given by the balance relation

$$\hat{\rho}^A = \frac{m^A}{V}\frac{d\left[(1-x)\,f_{int}\right]}{dt}, \tag{1.1}$$

where $\hat{\rho}^A$ denotes the intensity of mass source per unit time, and unit macroscopic volume.

In order to construct the model we have to specify the rates in this relation.

For $\frac{dx}{dt}$ we assume that changes of the fraction x are described by the Langmuir relation

$$\frac{dx}{dt} = a\,(1-x)\,p^A - bxe^{-\frac{E_b}{kT}}, \tag{1.2}$$

where p^A denotes the partial pressure of the adsorbate in the fluid phase, E_b is the energy barrier for particles adsorbed on the solid surface due to the van der Waals interaction forces, and it is assumed to be constant, a, and b are material parameters which within the present model may depend solely on the temperature, k is the Boltzmann constant, and T is the absolute temperature. In the case of full phase equilibrium we obtain from the equation (1.2) the following relation for the fraction of occupied sides

$$x_L = \frac{\frac{p^A}{p_0}}{1+\frac{p^A}{p_0}}, \qquad p_0 := \frac{b}{a}e^{-\frac{E_b}{kT}}, \tag{1.3}$$

which defines the so-called Langmuir isotherm.

The relation (1.3) indicates that within this model the isothermal equilibrium change of x can be produced by a change of partial pressure p^A. Such a change yields a new phase equilibrium with a new value of the equilibrium fraction x_L.

We proceed to formulate a relation for $\frac{df_{int}}{dt}$. We make the assumption that changes of the internal surface are coupled with dissipative changes of the porosity n which in turn describe relaxation processes of microscopic changes of volume of the skeleton. Latter processes are discussed in details in the works [1,2].

First of all let us notice that for sufficiently smooth internal surfaces of porous, and granular materials with a random geometry of pore spaces a change of an average characteristic linear dimension of the internal surface, and this of pores in the elementary representative volume can be assumed to be proportional: $\delta f_{int}^{\frac{1}{2}} \sim \delta\,(nV)^{\frac{1}{3}}$. Simultaneously dissipative changes of the porosity are given by a source $\hat{n}$ which describes the intensity of these changes per unit time and volume of the porous material. Bearing the above assumption in mind we obtain immediately

$$\frac{1}{f_{int}}\frac{df_{int}}{dt} = \varsigma\frac{\hat{n}}{n}, \tag{1.4}$$

where the proportionality factor ς is assumed to be constant for the purpose of this work.

Substitution of relations (1.2) and (1.4) in (1.1) yields

$$\hat{\rho}^A = \frac{m^A f_{int}}{V} be^{-\frac{E_b}{kT}}\left[x-(1-x)\frac{p^A}{p_0}+(1-x)\frac{\varsigma}{b}e^{\frac{E_b}{kT}}\hat{n}\right]. \tag{1.5}$$

Obviously in a thermodynamic phase equilibrium $\hat{n}\equiv 0$, and the fraction x is connected with the partial pressure p^A by the relation (1.3). Then the mass source vanishes identically.

In the next Section we incorporate this relation for changes of the fraction of bare sides into the continuum field model.

2. Continuum model of adsorption

Let us consider a porous body with a fluid component carrying the adsorbate (see: [3,4]). We assume that this fluid component and the adsorbate in the fluid phase have the same kinematics given by the field of velocity $\mathbf{v}^F(\mathbf{x},t)$. The skeleton (solid component) moves with the velocity $\mathbf{v}^S(\mathbf{x},t)$. If we denote by ρ^F, ρ^A, ρ^S the current mass densities of the fluid component, of the adosrbate, and of the skeleton, respectively, then the mass balance equations have the form

$$\begin{aligned} \frac{\partial \rho^S}{\partial t} + \operatorname{div}\left(\rho^S \mathbf{v}^S\right) &= -\hat{\rho}^A, \quad \frac{\partial \rho^F}{\partial t} + \operatorname{div}\left(\rho^F \mathbf{v}^F\right) = 0, \\ \frac{\partial \rho^A}{\partial t} + \operatorname{div}\left(\rho^A \mathbf{v}^F\right) &= \hat{\rho}^A. \end{aligned} \tag{2.1}$$

It has been assumed that the fluid component does not exchange the mass with other components.

These equations can be conveniently written in the following form

$$\begin{aligned} \frac{\partial \rho^S}{\partial t} + \operatorname{div}\left(\rho^S \mathbf{v}^S\right) &= -\rho^L \hat{c}, \quad \frac{\partial \rho^L}{\partial t} + \operatorname{div}\left(\rho^L \mathbf{v}^F\right) = \rho^L \hat{c}, \\ \frac{\partial c}{\partial t} + \mathbf{v}^F \cdot \operatorname{grad} c &= (1-c)\,\hat{c}, \end{aligned} \tag{2.2}$$

where we have introduced the notation

$$\rho^L := \rho^F + \rho^A, \qquad c := \frac{\rho^A}{\rho^F + \rho^A}, \qquad \hat{c} := \frac{\hat{\rho}^A}{\rho^F + \rho^A}. \tag{2.3}$$

The momentum balance equations shall be used in the reduced form in which the partial stress tensors of fluid components are spherical. Then

$$\begin{aligned} \frac{\partial \rho^S \mathbf{v}^S}{\partial t} + \operatorname{div}\left(\rho^S \mathbf{v}^S \otimes \mathbf{v}^S - \mathbf{T}^S\right) &= -\hat{\mathbf{p}}, \\ \frac{\partial \rho^L \mathbf{v}^F}{\partial t} + \operatorname{div}\left(\rho^L \mathbf{v}^F \otimes \mathbf{v}^F + p^L \mathbf{1}\right) &= \hat{\mathbf{p}}, \end{aligned} \tag{2.4}$$

where p^L is the partial pressure in the liquid (i.e. in the fluid and adsorbate in the fluid phase together), and it is assumed to be the sum of partial pressures in the fluid p^F, and in the adsorbate p^A: $p^L = p^F + p^S$. $\mathbf{T}^S$ denotes the partial Cauchy stress tensor in the skeleton, and $\hat{\mathbf{p}}$ is the momentum source in the liquid.

In addition to the above partial balance equations of mass and momentum we need an equation for the porosity. It has been argued in my earlier works on the model of porous materials [1,2] that the porosity satisfies a balance equation of its own, vis.

$$\frac{\partial n}{\partial t} + \mathbf{v}^S \cdot \operatorname{grad} n + n_E \operatorname{div}\left(\mathbf{v}^F - \mathbf{v}^S\right) = \hat{n}, \tag{2.5}$$

where n_E denotes an equilibrium value of the porosity. An assumption on small deviations from the thermodynamic equilibrium yields the following form of the source of porosity

$$\hat{n} = -\frac{\Delta}{\tau}, \qquad \Delta := n - n_E, \qquad \tau > 0, \tag{2.6}$$

where τ is the *relaxation time of porosity*. We accept this relation for the purpose of this work.

We proceed to construct the mass source $\hat{\rho}^A$ in the case of the above model of porous, and granular materials. Bearing the relation (1.5) in mind we obtain

$$\begin{aligned} \hat{\rho}^A &= \rho^A_{ad}\frac{1}{\tau_{ad}}\left[x - (1-x)\,\frac{cp^L}{p_0} - (1-x)\,\nu\Delta\right], \\ \rho^A_{ad} &:= \frac{m^A f_{int}}{V}, \quad \tau_{ad} := \frac{1}{b}e^{\frac{E_b}{kT}}, \quad \nu := \frac{\varsigma\tau_{ad}}{\tau}, \end{aligned} \tag{2.7}$$

where ρ^A_{ad} shall be assumed to be constant. It means that we neglect a small deviation of f_{int} from its reference value which seems to be reasonable in the case of small concentration c of the adsorbate. For the same reason we have made the assumption $p^A = cp^L$. τ_{ad} has the obvious interpretation of the *characteristic time of adsorption.*

In addition the fraction x must satisfy the evolution equation (1.2), i.e.

$$\frac{dx}{dt} + \left[x - (1-x)\,\frac{cp^L}{p_0}\right]\frac{1}{\tau_{ad}} = 0, \quad x_{t=0} = x_L \equiv \frac{\frac{cp^L_0}{p_0}}{1+\frac{cp^L_0}{p_0}}, \tag{2.8}$$

where p^L_0 denotes the reference value of the pressure in the liquid.

This completes the model of the mass source for adsorption.

The source $\hat{c}$ of equations (2.2) can be written in the form

$$\hat{c} = \frac{\rho^A_{ad}}{\rho^L}\left\{\left(x - (1-x)\,\frac{cp^L}{p_0}\right) - (1-x)\,\nu\Delta\right\}\frac{1}{\tau_{ad}}, \tag{2.9}$$

with x satisfying the evolution equation (2.8), and Δ satisfying the balance equation (2.5).

Bearing the above considerations in mind we can construct the model in the following way. If we denote by $\boldsymbol{\epsilon}^S$ the Almansi-Hamel tensor of small deformations of the skeleton then for the fields

$$\left\{\rho^S, \rho^L, c, n, \xi, \mathbf{v}^F, \mathbf{v}^S, \boldsymbol{\epsilon}^S\right\}, \qquad \frac{\partial\boldsymbol{\epsilon}^S}{\partial t} = \operatorname{sym}\left(\operatorname{grad}\mathbf{v}^S\right), \tag{2.10}$$

of a mechanical model of adsorption (isothermal processes) we need constitutive relations for the partial Cauchy stress tensor in the skeleton, $\mathbf{T}^S$, partial pressure, p^L, and the momentum source $\hat{\mathbf{p}}$. In the next Section we consider solely a very simple example of such relations.

3. Governing equations for a one-dimensional homogeneous process

In this Section we consider a homogeneous process of a one-dimensional compression of a three-component system in an impermeable cylinder. One of the components is an adsorbate with a small concentration c. The process is controlled by an impermeable piston at $z = 0$ on which the external pressure is changed from $p^0_{ext} = const.$ to $p_{ext} = const.$ Then the velocities $\mathbf{v}^S$, and $\mathbf{v}^F$ possess a one identical non-zero component, v_z, in the direction of the piston motion z, and this is a linear function of the coordinate z. The set of equations presented in the previous Section reduces to the following one

$$\begin{aligned}
\frac{\partial c}{\partial t} &= (1-c)\,\hat{c}, \quad \frac{\partial \rho^L}{\partial t} + \rho^L \frac{\partial \epsilon^S}{\partial t} = \rho^L \hat{c}, \\
&\Longrightarrow \quad \frac{\partial}{\partial t}\left(\ln \frac{\rho^L\,(1-c)}{\rho^L_0\,(1-c_0)} + \epsilon^S\right) \equiv \frac{\partial}{\partial t}\left(\ln \frac{\rho^F}{\rho^F_0} + \epsilon^S\right) = 0, \\
\frac{\partial \rho^S}{\partial t} + \rho^S \frac{\partial \epsilon^S}{\partial t} &= -\rho^L \hat{c}, \quad \frac{\partial \epsilon^S}{\partial t} = \frac{\partial v_z}{\partial z}, \quad \frac{\partial p^L}{\partial z} = 0, \quad \frac{\partial \sigma^S}{\partial z} = 0, \\
p^A &= c p^L.
\end{aligned} \tag{3.1}$$

In the above equations, ρ^L_0, and c_0 are reference values of ρ^L, and c, respectively, σ^S is the normal component in the z-direction of the stress tensor $\mathbf{T}^S$, and ϵ^S denotes the elongation of the skeleton in the z-direction, and it is the only essential component of the Almansi-Hamel deformation tensor $\boldsymbol{\epsilon}^S$.

In addition to the above relations we use the balance equation of porosity which serves the purpose of a field equation for the porosity n, and the evolution equation (2.10) for the field ξ.

In the case of homogeneous processes the porosity equation reduces to the evolution equation of the form

$$\begin{aligned}
\frac{\partial \Delta}{\partial t} &= -\frac{\Delta}{\tau} \qquad \Longrightarrow \qquad \Delta = (n_0 - n_E)\, e^{-\frac{t}{\tau}} \\
&\Longrightarrow \qquad n = n_E + (n_0 - n_E)\, e^{-\frac{t}{\tau}},
\end{aligned} \tag{3.2}$$

where n_0 is the initial value of the porosity, i.e. $\Delta_{t=0} = n_0 - n_E$. Let us notice that in the case of a natural initial condition for n when $n_0 = n_E$ the porosity remains constant in the whole process. This is due to the lack of diffusion in our simple example. However we can also expect an initial disturbance of porosity due to the coupling with deformation processes. We present this problem in the sequel.

In order to transform equations (3.1) into field equations for the fields

$$\left\{\rho^S, \rho^L, c, \epsilon^S\right\}, \tag{3.3}$$

we have to add constitutive relations for the quantities

$$\left\{\hat{c}, p^L, \sigma^S\right\}. \tag{3.4}$$

Let us notice that the common trivial kinematics of components of this example reduces the momentum balance equations to equilibrium conditions. On the other hand the usual boundary conditions for the one-dimensional case of the model of porous materials yield the following solution

$$\left.\begin{array}{c} \left(p^L - \sigma^S\right) = p_{ext} \quad \text{for } z = 0, \\ \rho^L \left(\mathbf{v}^F - \mathbf{v}^S\right) \cdot \mathbf{n} = \alpha \left(p^L - n p_{ext}\right) \quad \text{for } z = 0, \end{array}\right\} \tag{3.5}$$

$$\Longrightarrow \quad \left\{\begin{array}{c} p^L = n p_{ext} \\ \sigma^S = -\left(1-n\right) p_{ext}, \end{array}\right.$$

The coefficient α describes the so-called *surface permeability* (see: [3,4]) and it is immaterial in the present homogeneous case.

To close the set of equations we need constitutive relations for the source $\hat{c}$, the partial pressure p^L, and for the partial stress σ^S. The first one is given by the relation (2.9). The remaining two relations are assumed to be linear, and to have the form [1,2]

$$\begin{aligned} p^L &= n_0 p^0_{ext} + \varkappa^L(n)\left(\rho^L - \rho^L_0\right) + \beta\Delta, \\ \sigma^S &= -\left(1-n_0\right) p^0_{ext} + E^S(n)\,\epsilon^S + \beta\Delta, \end{aligned} \tag{3.6}$$

where the *compressibility coefficient* $\varkappa^L$ of the fluid, and the *elasticity coefficient* E^S of the skeleton may still depend on the current value of porosity. In the above relations β denotes the *coupling coefficient* of components.

Let us notice that constitutive relations (3.6) overdetermine the system of equations due to the simplification of kinematics assumed for the present example. Namely bearing equations (3.1) in mind we have to find solely the elongation ϵ^S from, say, equation $(3.6)_2$.

The first relation (3.6) should be identically satisfied which, of course, cannot be the case because $\varkappa^L(n)$ may be different for different materials. Consequently, we are not able to satisfy either the boundary condition $(3.5)_2$ or separately two constitutive relations (3.6). In the first case we would have to consider jointly both momentum balance equations, i.e.

$$\frac{\partial\left(p^L - \sigma^S\right)}{\partial z} = 0 \qquad \Longrightarrow \qquad p^L - \sigma^S = p_{ext}. \tag{3.7}$$

In the second case we would have to require solely

$$\begin{aligned} p^L - \sigma^S &= p^0_{ext} - E^S(n)\,\epsilon^S + \varkappa^L(n)\left(\rho^L - \rho^L_0\right) \quad \Longrightarrow \\ &\Longrightarrow \quad \epsilon^S = -\frac{1}{E^S(n)}\left\{\left(p_{ext} - p^0_{ext}\right) - \varkappa^L(n)\left(\rho^L - \rho^L_0\right)\right\}. \end{aligned} \tag{3.8}$$

For the purpose of this work we choose the second possibility.

However we still use (3.6) for the motivation of initial conditions needed to solve $(3.1)_{1,2,4}$ and (3.2). We have to specify the following initial conditions

$$\left\{\rho^L_{t=0}, c_{t=0}, \rho^S_{t=0}, \epsilon^S_{t=0}, \Delta_{t=0}\right\}. \tag{3.9}$$

These are not independent if we accept (3.6) for $t = 0$. If we choose $c_{t=0}$ and $\epsilon^S_{t=0}$ as given then we have

$$\begin{aligned}
\Delta_{t=0} &= -\frac{1}{\beta}\left\{(1-n_0)\left(p_{ext}-p^0_{ext}\right) - E^S(n_0)\,\epsilon^S_{t=0}\right\},\\
\rho^L_{t=0} &= \rho^L_0 + \frac{1}{\varkappa^L(n_0)}\left\{\left(p_{ext}-p^0_{ext}\right) + E^S(n_0)\,\epsilon^S_{t=0}\right\},\\
\rho^S_{t=0} &= \rho^S_0 J^{S-1}_{t=0} \cong \rho^S_0\left(1-\epsilon^S_{t=0}\right),
\end{aligned} \tag{3.10}$$

where J^S describes, as usual, changes of volume of the skeleton.

The choice of the initial condition for $\epsilon^S_{t=0}$ means that the full deformation of the skeleton ϵ^S consists of the instantaneous elastic deformation $\epsilon^S_{t=0}$ caused by the change of pressure $p^0_{ext} \to p_{ext}$ at $t = 0$, and of the "viscous" part $\left(\epsilon^S - \epsilon^S_{t=0}\right)$ which is due to the relaxation of porosity, and adsorption.

We are now in the position to formulate the main equation of the model, i.e. the equation $(3.1)_1$ for the concentration c. In order to simplify the numerical evaluation we assume additionally that small changes of the mass density ρ^L allow to replace it by ρ^L_0 in the coefficient of $\hat{c}$ (see: (2.9). We can neglect as well the fraction x in coefficients in which it is added to unity. This is admissible for small concentrations. These simplifications do not change qualitatively the results.

After easy manipulations we obtain the following equation

$$\frac{dc}{dt} + \gamma_1 c - \gamma_2 c^2 = \gamma_3, \quad c_{t=0} = c_0, \tag{3.11}$$

where

$$\begin{aligned}
\gamma_1 &:= \frac{\rho^A_{ad}}{\rho^L_0}\left[\frac{np_{ext}}{p_0} + x - \nu\Delta\right]\frac{1}{\tau_{ad}},\\
\gamma_2 &:= \frac{\rho^A_{ad}}{\rho^L_0}\frac{1}{\tau_{ad}}\frac{np_{ext}}{p_0}, \quad \gamma_3 := \frac{\rho^A_{ad}}{\rho^L_0}(x-\nu\Delta)\frac{1}{\tau_{ad}},
\end{aligned} \tag{3.12}$$

and the change of fraction x is given by the equation (2.8), whereas n, and Δ are given by the relations (3.2).

The set of equations for x and c is a coupled nonlinear set of differential equations which cannot be solved analytically. Therefore we use an iteration following from the assumption on a small value of the concentration c. Namely we integrate first the equation (2.8) with c replaced by c_0 which is a constant. Then we substitute this result in the equation (3.11) which becomes the Riccati equation, and can be solved approximately for small changes of the concentration. In the next iteration step we should substitute the solution of the Riccati equation in (2.8), and calculate x again. This would yield the next iteration step for c. For the purpose of this work we estimate only the first iteration step.

Bearing the solution (3.2) in mind we obtain for x

$$x = x_L - \exp\left[-g\left(t\right)\right] * \int_0^t \left[x_L - \left(1 - x_L\right) \frac{c_0 n\left(s\right) p_{ext}}{p_0}\right] \frac{\exp g\left(s\right)}{\tau_{ad}} ds, \quad (3.13)$$

$$g\left(t\right) := \left(1 + \frac{c_0 n_E p_{ext}}{p_0}\right) \frac{t}{\tau_{ad}} + \frac{\tau}{\tau_{ad}} \frac{c_0 p_{ext}}{p_0} \left(n_0 - n_E\right) \left(1 - e^{-\frac{t}{\tau}}\right).$$

It follows easily for large times

$$x = x_L + \frac{x_L - \left(1 - x_L\right) c_0 n_E \frac{p_{ext}}{p_0}}{1 + c_0 n_E \frac{p_{ext}}{p_0}} \left\{\exp\left[-\left(1 + c_0 n_E \frac{p_{ext}}{p_0}\right) \frac{t}{\tau_{ad}}\right] - 1\right\}, \quad i.e.$$

$$x \underset{t \longrightarrow \infty}{=} \frac{c_0 n_E \frac{p_{ext}}{p_0}}{1 + c_0 n_E \frac{p_{ext}}{p_0}}. \quad (3.14)$$

The last result means, of course, that the system relaxes to the point of Langmuir isotherm defined by a new value of the external loading. This limit is independent of the behaviour of porosity because $\Delta \underset{t \longrightarrow \infty}{=} 0$.

We proceed to investigate the first step in the approximation of the concentration. It follows easily from the equation (3.11)

$$\frac{d\left(c - c_0\right)}{dt} + \left(\gamma_1 - 2c_0\gamma_2\right) \frac{\rho_{ad}^A}{\rho_0^L} \frac{1}{\tau_{ad}} \left(c - c_0\right) = \gamma_3 - \gamma_1 c_0 + \gamma_2 c_0^2. \quad (3.15)$$

Certainly, this linear equation can be solved analytically. Bearing in mind a very small value of the relaxation time of porosity τ we can further simplify the solution of this equation, and after easy calculations we obtain

$$c = c_0 - \frac{\rho_{ad}^A}{\rho_0^L} \left[\frac{c_0 n_E p_{ext}}{p_0} \left(1 - e^{-\frac{t}{\tau_{ad}}}\right) + \frac{\nu\tau\left(n_0 - n_E\right)}{\tau_{ad}} \left(1 - e^{-\frac{t}{\tau}}\right)\right]. \quad (3.16)$$

Consequently the second contribution (i.e. influence of changes of porosity) is almost constant for $t > 0$, and it is equal to zero for $t = 0$. Its order of magnitude is the same as this of the first contribution (due to changes of fraction of occupied sides) provided the coefficient ν in the product with $\frac{\tau}{\tau_{ad}}$ is of the order of magnitude one, i.e. ς of the relation (1.4) is of the order of magnitude one.

4. Numerical example

In order to illustrate the qualitative behaviour of characteristic fields we present below a numerical example for typical data of real soils. These are presented in the table.

Table 1

Elastic constant, $E^S(n_E)$	40 GPa	Compressibility coeff., $\varkappa^L(n_E)$	$10^6\ \frac{\mathrm{m}^2}{\mathrm{s}^2}$
Coupling constant, β	100 MPa	Langmuir pressure, p_0	10 kPa
Initial concentration, c_0	10^{-3}	Initial porosity, n_0	0.23
Initial pressure, p^0_{ext}	100 kPa	Initial mass density, $\rho^L_0 \times 10^{-3}$	$0.23\ \frac{\mathrm{kg}}{\mathrm{m}^3}$
Relaxation time, τ	10^{-6} s	Charact. time of adsorp., τ_{ad}	1 s
mass density on f_{ad}, m^A	$7 \times 10^{-3}\ \frac{\mathrm{kg}}{\mathrm{m}^2}$	internal surface, $\frac{f_{int}}{V}$	$1500\ \frac{\mathrm{m}^2}{\mathrm{m}^3}$

In addition we choose $\epsilon^S_0 = -10^{-6}$, $\nu = 10^6$, and the loading pressure $p_{ext} = 200$ kPa.

For the above data we obtain the following time behaviour of the fraction x of occupied sides of the internal surface.

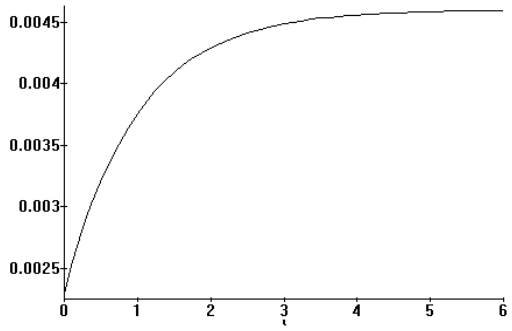

Fig. 1: Fraction x as a function of time $\frac{t}{\tau_{ad}}$

In Figure 2 we show the time behaviour of the concentration c described by the solution of the equation (3.15).

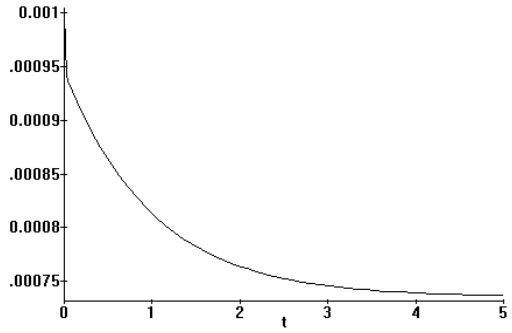

Fig. 2: Time changes of concentration c

The initial rapid change of the concentration is, of course, caused by the contribution of changing porosity. For $t = 0$ this contribution in the brackets of (3.16) is zero, and then grows rapidly to a constant value 0.00117, while the contribution of the changes of occupied sides grows slowly , and it reaches the maximum value of 0.00462 for $t \to \infty$.

In spite of simplicity and, consequently, some inconsistencies following from the lack of relative motion of components the above example shows clearly that the structure of mass balance proposed in this work for adsorption processes in porous, and granular materials

yields physically and mathematically reasonable results. It remains to be checked if it agrees quantitatively with experimental data. The latter problem is rather involved as discrepancies in available experimental data are very large indeed, and they cannot be clearly interpreted without a consistent model. The present model shows that such processes require estimates of at least five parameters specific for adsorption. Namely we need to know two relaxation times, τ, τ_{ad}, the coefficient ρ_{ad}^{A}, the coefficient ν, and the Langmuir pressure p_0. Only rough estimates are available for some simple physical systems.

References

1. K. Wilmanski; Porous Media at Finite Strains. The New Model With the Balance Equation For Porosity, *Arch. Mech.*, **48**, 4, 591-628 (1996).

2. K. Wilmanski; A Thermodynamic Model of Compressible Porous Materials with the Balance Equation of Porosity, *Transport in Porous Media*, **32:**, 21-47 (1998).

3. B. Albers; Coupling of Adsorption and Diffusion in Porous and Granular Materials. A 1-D Example of the Boundary Value Problem, *ZAMM* (1999, in preparation).

4. B. Albers, K. Wilmanski; Modeling of Adsorption and Diffusion in Multicomponent Continua, *Transport in Porous Media* (1999, in preparation).

5. I. Langmuir; The Constitution and Fundamental Properties of Solids and Liquids. Part 1, *J.Am.Chem.Soc.*,**38**, 2221-2295 (1916),

6. I. Langmuir; The Constitution and Fundamental Properties of Solids and Liquids. Part2, *J.Am.Chem.Soc.*, **39**, 1848 (1917),

7. I. Langmuir; The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum, *J.Am.Chem.Soc.,* **40,** 1361-1403 (1918).

8. D. A. Frank-Kamenetzki; *Stoff- und Wärmeübertragung in der chemischen Kinetik*, Springer, Berlin (1959).

9. S. J. Gregg, K. S. W. Sing; *Adsorption, Surface Area and Porosity*, Academic Press, London.(1982).