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On Adsorption and Diffusion in Porous Media

Bettina Albers[1]

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[1] Weierstrass Institute
for Applied Analysis
and Stochastics
Mohrenstr. 39
D – 10117 Berlin
Germany
E-Mail: albers@wias-berlin.de

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Dedicated to Prof. K. Wilmanski on the occasion of his 60th birthday.

Edited by
Weierstraß–Institut für Angewandte Analysis und Stochastik (WIAS)
Mohrenstraße 39
D — 10117 Berlin
Germany

Fax: + 49 30 2044975
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World Wide Web: http://www.wias-berlin.de/

Abstract

The paper contains a macroscopic continuum model of adsorption in porous materials consisting of three components. We consider the flow of a fluid/adsorbate mixture through channels of a solid component. The fluid serves as carrier for an adsorbate whose mass balance equation contains a source term. This term consists of two parts: first a Langmuir contribution which is connected with bare sites on internal surfaces and describes the Langmuir isotherm in equilibrium. The second one is due to changes of the internal surface driven by the source of porosity which is a part of the balance equation for porosity. We clearly state the range of applicability of the model. A simple numerical example which describes the transport of pollutants in soils illustrates the coupling of adsorption and diffusion. The results show that after a certain time arises a maximum in the rate of adsorption as a function of fluid/adsorbate velocity.

1 Introduction

The intention of this work is the theoretical, continuum mechanical approach to adsorption processes which appear quite often in nature. Examples are the pollution transport with rainwater in soil (organic materials like pesticides in agriculture, heavy metals in the subsoil of filling stations), tips where salts of industry and households are transported, the storage of atomic waste in salt layers or the penetration of moisture in plaster and concrete.

Although the mass exchange in these examples may also be driven by chemical processes in this work we consider physical adsorption processes. This means that particles of the adsorbate stick to the skeleton due to weak van der Waals forces. The type of mass exchange between fluid and skeleton (adsorption, chemisorption, capillary effects) mainly depends on two factors namely the particle size of the solid and the concentration of the adsorbate in the fluid.

For our model we consider very low adsorbate concentration. This entitles us to use the LANGMUIR theory of adsorption (see: [5]). It is based on the concept of the number of bare and occupied sites on the surface of a solid. Langmuir assumed that the adsorbate particles settle down on the solid in one single layer, and that there is a certain number of places where they are able to settle down. Obviously this is only possible if the adsorbate concentration is small. Otherwise the Langmuir isotherm of occupied sites reaches saturation. In the past many modifications of this theory appeared. One of them is the BET-model (see: [3]) which is based on the

Langmuir theory but allows mulitlayer adsorption. For our purpose there is no need to use this more complicated version of the Langmuir model because we assume low concentrations. In addition it should be mentioned that there are some doubts concerning the description of multilayer adsorption.

One of the important factors for the shape of the adsorption isotherm is the size of solid particles in relation to the pore size between them. According to GREGG/SING [4] there occur six types of adsorption isotherms. The three most important of them are shown in the figure below.

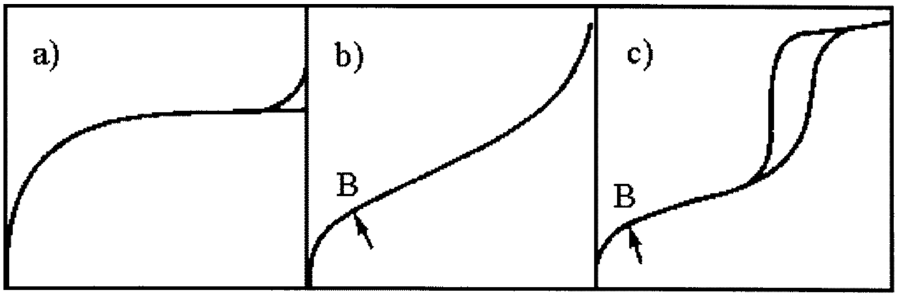

Fig. 1: Three most important types of adsorption isotherms (adsorbed amount vs. relative partial pressure)

The first one a) is the graph of the common monolayer Langmuir isotherm. In principle it describes the adsorption of particles on plane surfaces. But it also holds in our case because the pore size of the soil under consideration is big enough for the curvature of the pores not to play any important role. This is different in the case of isotherm c). This form of isotherm arises in case of the so-called mesopores (20-500 Å in diameter). Both b) and c) describe multilayer adsorption processes which is indicated by the existence of the inflection point B. Before reaching this point the monolayer process runs according the Langmuir isotherm i.e. adsorption is restricted to a thin layer on the walls. After that b) and c) show different behaviour. Although in both cases the slope increases, in b) the rise first is approximately linear and then rather rapid for higher relative pressures while in c) the amount adsorbed possesses another inflection point before the saturation vapour pressure is reached. A characteristic feature of c) is its hysteresis loop. This is due to the capillary condensation in the finest pores.

Summing up our model is intended to describe monolayer adsorption with low concentrated adsorbate on a porous medium with relatively large pores. Then the Langmuir isotherm looks as shown in a).

2 Three-dimensional adsorption/diffusion model

We investigate a flow of a fluid-adsorbate mixture through channels of a porous medium. Particles of adsorbate settle down on the internal surface of the skeleton so that their kinematics changes from that of the fluid to that of the skeleton. Fluid and adsorbate flow with a common velocity $\mathbf{v}^F$ through the skeleton which has the velocity $\mathbf{v}^S$. Fluid, adsorbate and skeleton have the current mass densities ρ^F, ρ^A and ρ^S, respectively. Then the mass balance equations have the form

$$\begin{aligned} \frac{\partial \rho^S}{\partial t} + \operatorname{div}\left(\rho^S \mathbf{v}^S\right) &= -\hat{\rho}^A, \\ \frac{\partial \rho^F}{\partial t} + \operatorname{div}\left(\rho^F \mathbf{v}^F\right) &= 0, \\ \frac{\partial \rho^A}{\partial t} + \operatorname{div}\left(\rho^A \mathbf{v}^F\right) &= \hat{\rho}^A, \end{aligned} \tag{1}$$

where $\hat{\rho}^A$ denotes the intensity of the mass source. We use the following definitions

$$\rho^L := \rho^F + \rho^A, \qquad c := \frac{\rho^A}{\rho^F + \rho^A}, \qquad \hat{c} := \frac{\hat{\rho}^A}{\rho^F + \rho^A}, \tag{2}$$

to transform the balances (1) in the following ones containing quantities related to the concentration

$$\begin{aligned} \frac{\partial \rho^S}{\partial t} + \operatorname{div}\left(\rho^S \mathbf{v}^S\right) &= -\rho^L \hat{c}, \\ \frac{\partial \rho^L}{\partial t} + \operatorname{div}\left(\rho^L \mathbf{v}^F\right) &= \rho^L \hat{c}, \\ \frac{\partial c}{\partial t} + \mathbf{v}^F \cdot \operatorname{grad} c &= (1 - c)\, \hat{c}. \end{aligned} \tag{3}$$

The momentum balance equations have the form

$$\begin{aligned} \frac{\partial \rho^S \mathbf{v}^S}{\partial t} + \operatorname{div}\left(\rho^S \mathbf{v}^S \otimes \mathbf{v}^S - \mathbf{T}^S\right) &= \hat{\mathbf{p}}, \\ \frac{\partial \rho^L \mathbf{v}^F}{\partial t} + \operatorname{div}\left(\rho^L \mathbf{v}^F \otimes \mathbf{v}^F + p^L \mathbf{1}\right) &= -\hat{\mathbf{p}}, \end{aligned} \tag{4}$$

where the partial stress tensors of fluid components are spherical. The partial pressure in the liquid phase p^L (i.e. in the fluid and adsorbate phases together) is the sum of the partial pressures in the fluid p^F, and in the adsorbate p^A. According to Dalton's law we expect that $p^A \cong cp^L$. This relation holds if the concentration of the adsorbate in the fluid is small as assumed in our case. Furthermore $\mathbf{T}^S$ denotes the partial Cauchy stress tensor in the skeleton, and $\hat{\mathbf{p}} = \pi \left(\mathbf{v}^F - \mathbf{v}^S\right) - \rho^L \hat{c} \mathbf{v}^F$ is the momentum source in the liquid where π denotes the permeability coefficient.

For the scalar field of porosity we have an additional balance equation as introduced in e.g. [6]. For small deformations of the skeleton it has the form

$$\frac{\partial n}{\partial t} + \mathbf{v}^S \cdot \operatorname{grad} n + n_E \left(\mathbf{v}^F - \mathbf{v}^S\right) = \hat{n} = -\frac{\Delta}{\tau}. \tag{5}$$

Here $\Delta = n - n_E$ is the deviation of the porosity n from its equilibrium value n_E and τ is the *relaxation time of porosity.* The above shape of the source of porosity $\hat{n}$ is based on assumptions on small deviations from thermodynamic equilibrium.

3 Specification of the mass source

One of the most important factors for the extent of adsorption is the internal surface area of the solid. There exist numerous methods for quantitative evaluation of this area, e.g. through measurements of adsorption itself (see investigation of type c)-isotherms in [4]). For the purpose of the present work, where the skeleton is considered to be a soil, we lean on a value of the internal surface mentioned by J. Bear in [2].

Also the number of *bare* and *occupied sites* on the surface of the solid has imortant influence on the adsorbed amount. This quantities were introduced by I. Langmuir in his classical works on adsorption (e.g. [5]). On the macroscopic level of description i.e. within a representative elementary volume (REV) of a porous or granular material we denote the normalized fraction of occupied sites by ξ, i.e. the fraction of bare sites is $1-\xi$. REV is small in comparison with the volume of the whole flow regime but big against volumes of single pores of the skeleton. Furthermore we denote the internal surface area of the pores in REV by f_{int} which means that $\frac{f_{int}}{V}$ is the internal surface area per unit volume. The mass of adsorbate per unit of the internal surface area is m_A. Then the mass source is given by the relation

$$\hat{\rho}^A = -\frac{m^A}{V}\frac{d\left(\xi\, f_{int}\right)}{dt} = -\frac{m^A}{V}\left(f_{int}\frac{d\xi}{dt} + \xi\frac{d\,f_{int}}{dt}\right), \tag{6}$$

where V is the REV-volume. This relation describes the mass transfer rate from the liquid to the solid phase per unit time.

The first contribution on the right-hand side of this equation describes the change of the fraction of occupied sites. It is specified by the Langmuir evolution equation

$$\frac{d\xi}{dt} = a\left(1-\xi\right)p^A - b\xi e^{-\frac{E_b}{kT}}, \tag{7}$$

where p^A is the partial pressure of the adsorbate in the fluid phase and a and b are material parameters. The energy barrier E_b for particles adsorbed on the skeleton is assumed to be constant. Furthermore k denotes the Boltzmann constant and T is the absolute temperature.

The right hand side of Eq. (7) again consists of two terms: the adsorption rate (first term) and the desorption rate (second term). In full phase equilibrium they are equal so that the time change of occupied sites is equal to zero. In this case we get from (7) the well-known *Langmuir isotherm* of occupied sites

$$\xi_L = \frac{\frac{p^A}{p_0}}{1+\frac{p^A}{p_0}}, \quad \text{with} \quad p_0 := \frac{b}{a}e^{-\frac{E_b}{kT}}. \tag{8}$$

An isothermal equilibrium change of ξ can be produced by a change of partial pressure p^A. This yields a new phase equilibrium, i.e. another point on the Langmuir isotherm.

The other part of (6) describes the change of the internal surface. We assume that this change is coupled with relaxation of the porosity n, which is described by the balance equation of porosity (for detailed information about the new model for porous bodies with the balance equation of porosity see: WILMANSKI [6]). The source of porosity $\hat{n}$ describes the intensity of dissipative changes of porosity per unit time and volume of the porous material. Motivated by elementary considerations about changes of the internal surface and of the porosity in a porous medium yielding film adsorption (see [1]) we assume

$$\frac{1}{f_{int}} \frac{d f_{int}}{dt} \propto \frac{\hat{n}}{n}. \tag{9}$$

In the following we will illustrate the model by means of a simple example and point out the resulting coupling of adsorption and diffusion.

4 One-dimensional example

We consider the flow of a fluid-adsorbate mixture through a part of soil.

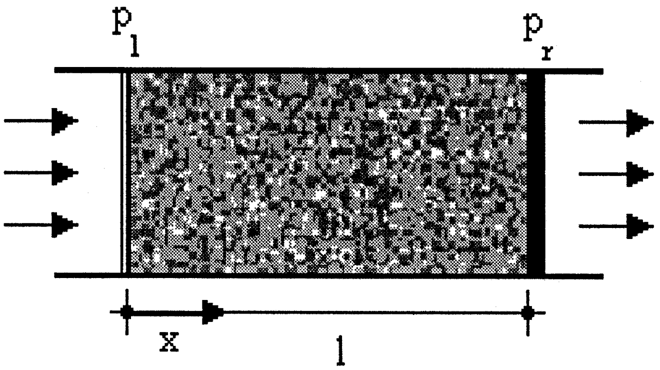

Fig. 2: Fluid-adsorbate mixture flows through a part of soil.

Due to a difference of the external pressure, with p_l at $x = 0$ being larger than p_r at $x = l$, the mixture flows along the direction x through the porous body. The low concentrated adsorbate is carried by the fluid and has therefore the same velocity v^F. Then the isothermal process is described by the fields

$$\left\{\rho^S, \rho^L, c, v^F, v^S, e^S, \Delta, \xi, f_{int}\right\}, \tag{10}$$

where apart from the customary fields for flow processes the last three are the above introduced additional fields describing mass exchange processes.

For the purpose of this example we make the following assumptions:

- the skeleton does not move, i.e. $v^S \equiv 0$,

- the inertia forces are small i.e. the acceleration terms in the momentum balances can be neglected,
- small changes in time of the velocity gradient, i.e. the porosity balance reduces to the algebraic relation

  $$\Delta \simeq -n_E \tau \frac{\partial v^F}{\partial x}.$$

  This follows from the assumption that the characteristic macroscopic time t is much larger than τ. The algebraic form of the relation for Δ bears also the positive consequence that we need no additional boundary condition for it.

4.1 Governing set of equations and constitutive relations

Under these assumptions and bearing in mind relations (6), (7) and (9) the source of concentration $\hat{c}$ can be written as

$$\hat{c} = -\frac{\rho^A_{ad}}{\rho^L} \left\{ \left[(1-\xi) \frac{cp^L}{p_0} - \xi \right] \frac{1}{\tau_{ad}} - \xi \frac{\nu}{\tau} \Delta \right\}, \tag{11}$$

where τ_{ad} denotes the characteristic time of adsorption, p_0 is a reference pressure of adsorption which is defined in (8) and it has been measured for instance by Langmuir (see: $[5]_3$), ν is a proportionality factor and $\rho^A_{ad} := \frac{m^A f_{int}}{V}$.

Then the balance equations have the following form

$$\frac{\partial \rho^L}{\partial t} + \frac{\partial \rho^L v^F}{\partial x} = -\rho^A_{ad} \left\{ \left[\frac{cp^L}{p_0} - \left(1 + \frac{cp^L}{p_0} \right) \xi \right] \frac{1}{\tau_{ad}} - \xi \frac{\nu}{\tau} \Delta \right\},$$

$$\frac{\partial c}{\partial t} + v^F \frac{\partial c}{\partial x} = -(1-c) \frac{\rho^A_{ad}}{\rho^L} \left\{ \left[\frac{cp^L}{p_0} - \left(1 + \frac{cp^L}{p_0} \right) \xi \right] \frac{1}{\tau_{ad}} - \xi \frac{\nu}{\tau} \Delta \right\}, \tag{12}$$

$$\frac{\partial p^L}{\partial x} + \pi v^F = 0, \qquad n_E \frac{\partial v^F}{\partial x} = -\frac{\Delta}{\tau},$$

$$\frac{\partial \xi}{\partial t} = \left[(1-\xi) \frac{cp^L}{p_0} - \xi \right] \frac{1}{\tau_{ad}}.$$

The relations for the skeleton are not showed, because they can be solved separately. The constitutive relation for the pressure in the liquid phase p^L is assumed to be

$$p^L = p^L_0 + \kappa \left(\rho^L - \rho^L_0 \right) + \beta \Delta, \tag{13}$$

where p^L_0 and ρ^L_0 are initial values of the pressure and the mass density for the liquid phase. κ denotes the compressibility coefficient and β is a material coupling parameter.

4.2 Initial and boundary conditions

We assume the following initial values for the fluid-/adsorbate velocity, the change of porosity, the mass density in the liquid phase, the pressure in the liquid phase, the concentration and the number of occupied sites, respectively

$$\begin{array}{ll} v^F(x,t=0)=0, & \Delta(x,t=0)=0, \\ \rho^L(x,t=0)=\rho_0^L, & p^L(x,t=0)=p_0^L\equiv n_E p_{ext}, \\ c(x,t=0)=c_0, & \xi(x,t=0)=\xi_L\equiv \frac{c_0\frac{p_0^L}{p_0}}{1+\frac{p_0^L}{p_0}}. \end{array} \tag{14}$$

The boundary conditions are assumed to be of third type. They express the flow through the boundary of the body in dependence on the difference of the partial pressure in the liquid and the part of the external pressure which acts on the fluid, as well as on the permeability α of the surface:

$$\begin{array}{rcll} x &=& 0: & -\rho^L v^F=\alpha\left(p^L-np_l\right), \\ x &=& l: & \rho^L v^F=\alpha\left(p^L-np_r\right). \end{array} \tag{15}$$

4.3 Regular perturbation solution and Laplace transform

We use regular perturbation method to find an approximate solution of the problem. We make the following linear ansatz

$$\begin{array}{c} \rho^L=\rho_0^L+\varepsilon\rho_1^L, \qquad v^F=\varepsilon v_1^F, \qquad \Delta=\varepsilon\Delta_1, \\ c=c_0+\varepsilon c_1, \qquad \xi=\xi_L+\varepsilon\xi_1. \end{array} \tag{16}$$

These expansions which depend on a small parameter ε are truncated after first order contributions. The definition of ε is based on the assumption that the pressure difference between the left and the right boundary

$$\varepsilon=\frac{p_l-p_r}{p_r}, \tag{17}$$

is small. The zeroth step of the perturbation is trivial i.e. ρ_0^L, c_0 and ξ_L are constants. For the first step we get the following set of equations

$$\begin{array}{l} \frac{\partial\rho_1^L}{\partial t}+\rho_0^L\frac{\partial v_1^F}{\partial x}=\rho_{ad}^A\left\{\left[\iota_1\xi_1-\iota_2c_1-\iota_3\rho_1^L-\iota_4\Delta_1\right]\frac{1}{\tau_{ad}}+\iota_5\Delta_1\right\}, \\ \frac{\rho_0^L}{\rho_{ad}^A}\frac{\partial c_1}{\partial t}=\Big\{-\iota_6c_1-\iota_7\rho_1^L+(1-c_0)\left[\iota_1\xi_1-\iota_2c_1-\iota_3\rho_1^L-\iota_4\Delta_1\right]\frac{1}{\tau_{ad}}+ \\ \qquad\qquad +(1-c_0)\,\iota_5\Delta_1\Big\}, \\ \kappa\frac{\partial\rho_1^L}{\partial x}+\beta\frac{\partial\Delta_1}{\partial x}+\pi v_1^F=0, \qquad\qquad \Delta_1=-n_E\tau\frac{\partial v_1^F}{\partial x}, \\ \frac{\partial\xi_1}{\partial t}=-\left[\iota_1\xi_1-\iota_2c_1-\iota_3\rho_1^L-\iota_7\Delta_1\right]\frac{1}{\tau_{ad}}, \end{array} \tag{18}$$

where we have used abbreviations

$$
\begin{aligned}
\iota_1 &:= 1 + \frac{c_0 p_0^L}{p_0}, \qquad \iota_2 := (1 - \xi_L)\,\frac{p_0^L}{p_0}, \\
\iota_3 &:= (1 - \xi_L)\,\frac{c_0 \kappa}{p_0}, \qquad \iota_4 := (1 - \xi_L)\,\frac{c_0 \beta}{p_0}, \\
\iota_5 &:= \xi_L \frac{\nu}{\tau}, \qquad \iota_6 := \xi_L - \frac{(1 - \xi_L)\, c_0 p_0^L}{p_0}, \\
\iota_7 &:= \frac{(1 - c_0)}{\rho_0^L}\left(\xi_L - \frac{(1 - \xi_L)\, c_0 p_0^L}{p_0}\right).
\end{aligned}
\tag{19}
$$

We use the following Laplace transforms to find an analytical solution of the linear problem

$$
\tilde{\rho}_1^L = \int_0^\infty \rho_1^L e^{-st} dt \quad \text{and analogous for } \tilde{v}_1^F, \tilde{\Delta}_1, \tilde{c}_1, \tilde{\xi}_1. \tag{20}
$$

The transformed quantities are functions of two variables (x, s). Provided Sommerfeld conditions for $t \to \infty$ are fulfilled we have according to the initial data

$$
\rho_1^L e^{-st}\Big|_0^\infty = 0 \quad \text{and analogous for } \tilde{v}_1^F, \tilde{\Delta}_1, \tilde{c}_1, \tilde{\xi}_1. \tag{21}
$$

We eliminate system (18) in order to obtain a differential equation for $\tilde{v}_1^F$ and get

$$
\begin{aligned}
\tilde{\Delta}_1 &= -n_E \tau \frac{\partial \tilde{v}_1^F}{\partial x}, \qquad \tilde{c}_1 = z_6 \frac{\partial \tilde{v}_1^F}{\partial x}, \\
\tilde{\xi}_1 &= z_7 \frac{\partial \tilde{v}_1^F}{\partial x} \quad \text{and} \quad \tilde{\rho}_1^L = z_8 \frac{\partial \tilde{v}_1^F}{\partial x},
\end{aligned}
\tag{22}
$$

where the coefficients z_i depend in different manner on the Laplace variable s :

$$
\begin{aligned}
z_1 &:= \frac{-\rho_0^L + \rho_{ad}^A n_E \tau\,(\iota_4 - \iota_5)}{s + \iota_3 \rho_{ad}^A}, \qquad z_2 := \frac{\rho_{ad}^A \iota_1}{s + \iota_3 \rho_{ad}^A}, \\
z_3 &:= \frac{\rho_{ad}^A \iota_2}{s + \iota_3 \rho_{ad}^A}, \qquad z_4 := \frac{\iota_3 z_1 - \iota_4 n_E \tau}{s + \iota_1 - \iota_3 z_2}, \qquad z_5 := \frac{\iota_2 - \iota_3 z_3}{s + \iota_1 - \iota_3 z_2}, \\
z_6 &:= \frac{-\iota_7(z_1 + z_2 z_4) + (1 - c_0)\,\iota_1 z_4 - (1 - c_0)\,\iota_3 (z_1 + z_2 z_4) + (1 - c_0)\, n_E \tau\,(\iota_4 - \iota_5)}{\frac{\rho_0^L}{\rho_{ad}^A} s + \iota_6 + \iota_7 (z_2 z_5 - z_3) - (1 - c_0)\,\iota_1 z_5 + (1 - c_0)\,\iota_2 + (1 - c_0)\,\iota_3 (z_2 z_5 - z_3)}, \\
z_7 &:= z_4 + z_5 z_6, \qquad z_8 := z_1 + z_2 z_7 - z_3 z_6.
\end{aligned}
\tag{23}
$$

Then we get the demanded equation for $\tilde{v}_1^F$

$$
\frac{\partial^2 \tilde{v}_1^F}{\partial x^2} - \frac{\pi}{\underbrace{\beta n_E \tau - \kappa z_8}_{a}}\, \tilde{v}_1^F = 0, \tag{24}
$$

from which we get the solution

$$
\begin{aligned}
\tilde{v}_1^F &= C_1 e^{\sqrt{a}x} + C_2 e^{-\sqrt{a}x}, \\
\tilde{\rho}_1^L &= z_8 \sqrt{a} \left(C_1 e^{\sqrt{a}x} - C_2 e^{-\sqrt{a}x} \right), \\
\tilde{\Delta}_1 &= -n_E \tau \sqrt{a} \left(C_1 e^{\sqrt{a}x} - C_2 e^{-\sqrt{a}x} \right), \\
\tilde{c}_1 &= z_6 \sqrt{a} \left(C_1 e^{\sqrt{a}x} - C_2 e^{-\sqrt{a}x} \right), \\
\tilde{\xi}_1 &= z_7 \sqrt{a} \left(C_1 e^{\sqrt{a}x} - C_2 e^{-\sqrt{a}x} \right).
\end{aligned}
\tag{25}
$$

To determine the integration constants we need expansions of the boundary conditions. Inserting the constitutive relation (13) for p^L into the boundary conditions (15) we obtain for the first step

$$
\begin{aligned}
-\rho_0^L v_1^F &= \alpha \left(\kappa \rho_1^L + \beta \Delta_1 - p_r \Delta_1 - n_E p_r \right) \Big|_{x=0}, \\
\rho_0^L v_1^F &= \alpha \left(\kappa \rho_1^L + \beta \Delta_1 - p_r \Delta_1 \right) \Big|_{x=l},
\end{aligned}
\tag{26}
$$

where the pressure on the left hand side of the channel p_l is defined by means of the given pressure on the right hand side p_r

$$
p_l := p_r + \varepsilon p_r, \qquad \varepsilon > 0. \tag{27}
$$

After applying the Laplace transform and inserting the solution (25) we have

$$
\begin{gathered}
-\rho_0^L \left(C_1 + C_2 \right) = z_9 \left(C_1 - C_2 \right) - \frac{\alpha n_E p_r}{s}, \\
\rho_0^L \left(C_1 e^{\sqrt{a}l} + C_2 e^{-\sqrt{a}l} \right) = z_9 \left(C_1 e^{\sqrt{a}l} - C_2 e^{-\sqrt{a}l} \right), \\
z_9 = \alpha \left[\kappa z_8 - n_E \tau \left(\beta - p_r \right) \right] \sqrt{a}.
\end{gathered}
\tag{28}
$$

and finally for the integration constants

$$
\begin{aligned}
C_1 &= -\frac{\alpha n_E p_r \left(z_9 + \rho_0^L \right)}{s \left[\left(z_9 - \rho_0^L \right)^2 e^{2\sqrt{a}l} - \left(z_9 + \rho_0^L \right)^2 \right]}, \\
C_2 &= -\frac{\alpha n_E p_r \left(z_9 - \rho_0^L \right) e^{2\sqrt{a}l}}{s \left[\left(z_9 - \rho_0^L \right)^2 e^{2\sqrt{a}l} - \left(z_9 + \rho_0^L \right)^2 \right]}.
\end{aligned}
\tag{29}
$$

In order to get numerical solutions for the inverse Laplace transform we use a FORTRAN-solver.

4.4 Results

To illustrate the above presented solution we choose the following parameters

Length of the body l	1 m
Initial mass density ρ_0^L	$2.3 \cdot 10^2\ \frac{\mathrm{kg}}{\mathrm{m}^3}$
Equilibrium porosity n_E	0.23
Initial concentration c_0	10^{-3}
Initial pressure p_0^L	23 kPa
Langmuir pressure p_0	10 kPa
Pressure on right h.s. p_r	100 kPa
Proportionality factor ν	10
Coupling constant β	1 GPa
Compressibility κ	$2.25 \cdot 10^6\ \frac{\mathrm{m}^2}{\mathrm{s}^2}$
Permeability of solid π	$10^9\ \frac{\mathrm{kg}}{\mathrm{m}^3\mathrm{s}}$
Permeability of surface α	$4 \cdot 10^{-8}\ \frac{\mathrm{s}}{\mathrm{m}}$
Relaxation time τ	10^{-3} s
Charact. time of adsorp. τ_{ad}	1 s
Fraction of occupied sites in equilibrium ξ_L	$2.3 \cdot 10^{-2}$
mass density of adsorbate on internal surface ρ_{ad}^A	$40\ \frac{\mathrm{kg}}{\mathrm{m}^3}$

Mass density and porosity have been chosen to have typical values for rocks and soils. The values for material parameters β and τ have been chosen on the basis of estimates of the attenuation of acoustic waves. The influence of permeability is expressed by two constants π and α. The first one describes the resistance of the skeleton to the flow of the fluid/adsorbate mixture. The second one describes the surface resistance to the outflow of the mixture from the solid. Its appearance is connected with a boundary layer between the porous body and the external world.

The following results are presented in the form of coefficients of ε, the normalized difference between the pressures on the left and the right hand side of the channel. For flow processes in soil we assume that $\varepsilon = 0.1$. This means that the pressure difference between both sides is one tenth of an atmospheric pressure.

In the figures below we present changes of various fields (i.e. (25)) as functions of place x for chosen values of time t. For the chosen value of characteristic time of adsorption τ_{ad} of 1 second we obtain a total time of 10 seconds for the whole adsorption process. However in reality the characteristic time of adsorption is of order of hours or days so that the real time scale of the process is also of that order.

Figure 3a) shows the change of the mass density of the liquid phase. It increases in time for all places of the channel but these increments are steeper at the beginning of the flow regime than at the end. At the left hand side of the channel it reaches a maximum value of about $1.5{\cdot}10^{-3}\ \frac{\mathrm{kg}}{\mathrm{m}^3}$, on the other side it is only one half of this value. The order of this quantity depends on the pressure difference between both sides.

In Figure 3b) we see the x-component of the common velocity of the fluid and the adsorbate. Also this field starts from zero at the beginning of the process. The linear line shows the shape which appears after short time: the velocity is nearly constant in time and linearly decreasing in place.

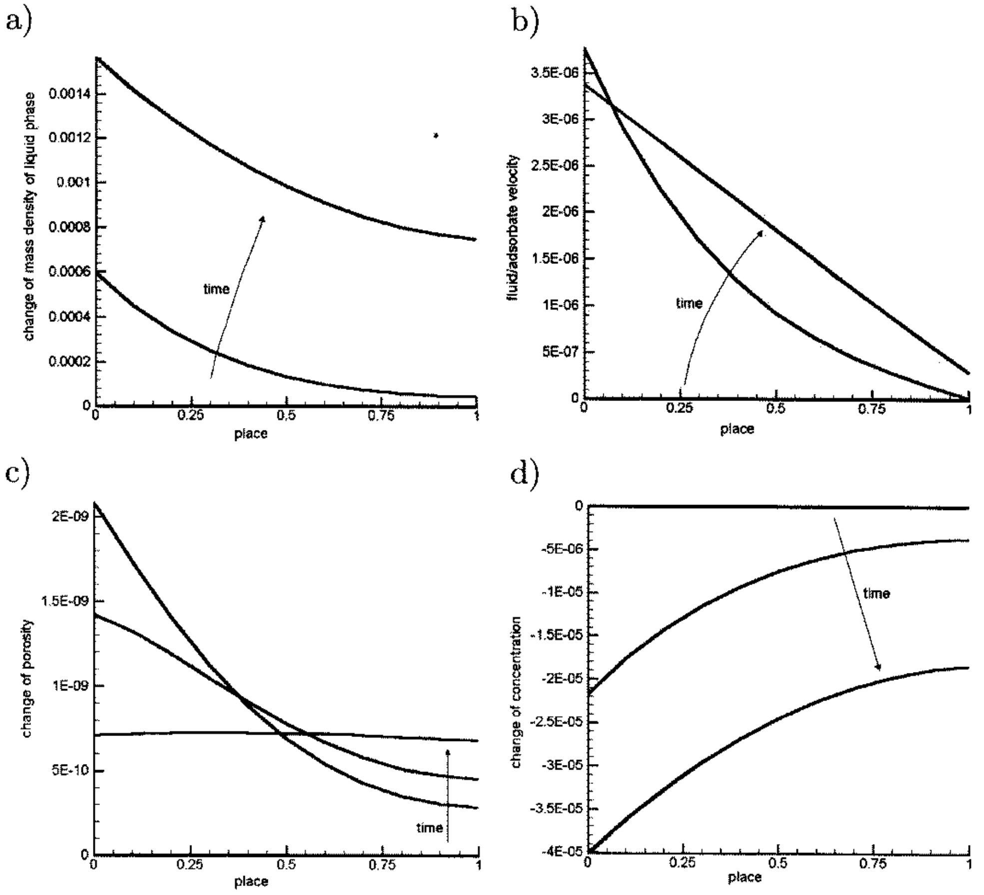

Fig. 3: a) Change of mass density of the liquid phase,
b) Velocity of fluid and adsorbate,
c) Change of porosity,
d) Change of concentration.

The algebraic form of the porosity balance yields a change of porosity from its equilibrium value proportional to the velocity gradient. Therefore this change is nearly constant after a short period of time. Whereas the increments in Fig. 3c) are very steep for the left hand side of the considered region they are almost negligible at the right hand side.

If particles of adsorbate settle down on the skeleton the concentration of the adsorbate in the liquid phase decreases, of course, in time as we can see in Fig. 3d). It starts with its initial value of 10^{-3} and the maximum change is $-4 \cdot 10^{-5}$. Also over the length of the body the concentration decreases. These increments are much steeper on the left hand side than on the right hand side. As concentration and the fraction of occupied sites are coupled, of course the fraction of occupied sites increases in the same manner as the concentration decreases (see: [1]).

The most important result of this work is the form of coupling of adsorption and diffusion. It is shown how the amount adsorbed (absolute value of the concentration source) depends on the relative velocity of the components. In Fig. 4 the source of concentration over the fluid/adsorbate velocity is shown. Due to the assumption that the skeleton does not move the fluid/adsorbat velocity in our case stands for the relative velocity of the components. As follows from the boundary conditions this quantity is mainly driven by the surface permeability parameter α.

The results shown in Fig. 4 are as follows. Firstly one can see the characteristic time behaviour of the intensity of adsorption. Its absolute value has a jump at the beginning of the process ($3.5 \cdot 10^{-5}$ – negative value is due to the reference to the fluid). Then this value diminishes until it reaches an asymptotic value of $1.5 \cdot 10^{-6}$. It can be seen better in the sequence of curves for different times shown in Fig. 5.

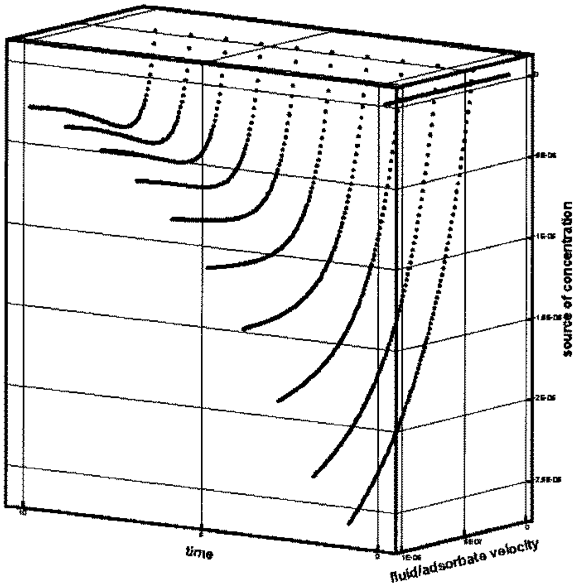

Fig. 4: Influence of diffusion.

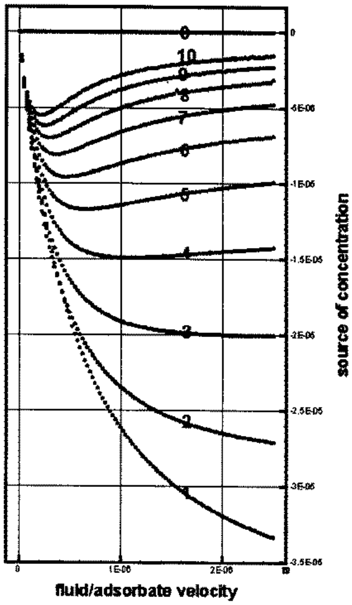

Fig. 5: Velocity dependence for several times.

The other important feature is the dependence on the relative velocity. This also depends on the progress of the process. At the beginning the absolute value of the source of concentration (i.e. the rate of adsorption) increases for every velocity and approaches an asymptotic value. However after a certain time lapse the curves possess a maximum which lies in the range of small velocities. With increasing time this maximum becomes stronger pronounced.

5 Conclusions

The main aim of this work was to show the dependence of adsorption on diffusion. This relation is not visible if we consider a particular choice of material parameters. For instance the changes in time of the rate of adsorption have an expected behaviour: After a jump at the initial instant of time they relax smoothly. However if we vary the relative velocity of components which in our case means a variation of the fluid/adsorbate velocity then for each velocity the behaviour is qualitatively the same but quantitatively there is a nonmonotonic dependence on the velocity. This is shown in the 3D picture which has been obtained by varying the surface permeability α. As we see, there is a region of relative velocities where the rate of adsorption reaches a maximum value. One can conclude that in the case of very small and very large diffusion the adsorption rate decays much faster than it is the case for moderate diffusion.

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