

INSIGHT INTO THE PROBLEMS OF MASS TRANSPORT MODELLING IN GRANULAR LAYER

ANNA ADACH, STANISŁAW WRÓŃSKI

Department of Chemical and Process Engineering, Warsaw Technical University
Waryńskiego 1, 00-645 Warsaw, Poland

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POGLĄD NA PROBLEMY MODELOWANIA TRANSPORTU MASY W ZŁOŻACH ZIARNISTYCH

W pracy przedstawiono skrótoowo problemy związane z modelowaniem migracji zanieczyszczeń w złożach ziarnistych. Ogólny model migracji przedstawiono w formie bezwymiarowej. Model podstawowy zaadoptowano do opisu praktycznej metody dekontaminacji, formułując dwa modele operacyjne, w zależności od dominujących oporów transportu masy w układzie. Weryfikacja modelu potwierdziła poprawność modelu i jego implementacji numerycznej w różnych warunkach. Potwierdza to możliwość praktycznego zastosowania metody do estymacji migracji zanieczyszczeń w złożach ziarnistych. Zasygnalizowano istotny wpływ nieregularności dystrybucji ujemnych źródeł masy na transport masy w układzie.

S u m m a r y

The short outlook at main problems related to pollutant migration modelling in the granular layer is critically discussed in the paper. The general model of pollutant migration in granular was transposed into dimensionless form. The general model was adapted to describe the examined decontamination technology and two operational models were differentiated due to the dominant mass transfer resistances in the system. The verification validated the functional effectiveness of the suggested model and its numerical implementation under different conditions. It approves the possibility of the practical application of the proposed method. The problem of influence of irregular distribution of negative mass sources (sorptive agglomerates) on mass transport in the granular layer was underlined.

APPROACHES OF MASS TRANSPORT MODELLING IN GRANULAR LAYER

Migration and adsorption of soluble substances in the granular media are frequently encountered in many natural and industrial processes (chromatography, catalytic reactors, enzymatic reactors etc.). In particular, it concerns also the cases of environmental importance such as migration of pollutants in solid wastes, soils, sludges, etc. The problem of the mutual interaction between contaminants and the soil or sewage sludge layer components, the mechanism and kinetics of migration of those substances, as well as chemical, physicochemical and biological methods of their degradation are complex issues, described in many monographs [27, 35].

The problems of migration and decontamination of pollutants caused that mathematical modelling of migration of substances in the granular layer can be divided into two main streams, depending on particular aims. The first models concern describing the migration and propagation of hazardous substances in the environment. This approach allows evaluating the existing hazard, the directions and speed of propagation of contaminants, and also predicting perspective risk assessment. The second approach bases on creating a model describing the processes of decontamination in the grain layer. This gives an opportunity to examine the influence of the particular factors, which are involved in the process, as well as to evaluate the effectiveness of the process and finally result in its optimisation.

In a broad literature concerning this problem there exist several different approaches to modelling mass transfer in the granular layer, depending on the particular aim and considered case. Therefore, the short outlook of the main concepts related to this issue is critically discussed below.

The approach, which assumes full saturation of the layer while formulating transport equation, can be frequently found in monographs. This formulation is obviously based on the Darcy's law and continuity equation for liquid phase.

$$q = -\frac{K_f}{\mu_l}(\nabla p - \rho g) \quad (1)$$

$$\frac{\partial(\epsilon\rho)}{\partial t} = -\nabla(q\rho) \quad (2)$$

Full saturation is often considered in works that incorporate the conventional convection-diffusion models (with sorption terms) for describing pollutant transport in porous media [43] and migration of radionuclides basing on compartmental model in fully saturated soil is examined in [20]. Mass transport for multi-species chemical system is described in [36]. In some works simplification in the form of full saturation of the layer is assumed in order to obtain analytical or numerical solution of mass transfer in complex system, e.g. one-dimensional problem of mass transfer, where the fluid flows through channels of medium accompanied by skeleton movement is described in [6].

The „partial saturation” approach in formulation of transport equation is usually used for describing the solute migration in the soils, especially if the changes of the water content appear in time (due to the flow, temperature, season etc.). These models base on the so-called Richards Equation, which describes a one-dimensional, vertical, unsaturated, transient water flow in a nondeformable porous medium, assuming negligible pressure gradient in the air phase [25, 28]. Richards equation in the water content takes the form [28]:

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial x} \left[K_h(\theta) \frac{dh_s}{d\theta} \frac{d\theta}{dx} \right] - \frac{\partial K_h(\theta)}{\partial x} + S_w(\theta) \quad (3)$$

Taking into account: $C_h(q) = dq / dh_s$ the equation was set in the matric potential form:

$$C_h \frac{\partial h_s}{\partial t} = -\frac{\partial}{\partial x} \left[K_h(h_s) \frac{\partial h_s}{\partial x} \right] - \frac{\partial K_h(h_s)}{\partial x} + S_w(h_s) \quad (4)$$

Several parameterisations of proper defining of the unsaturated soil hydraulic properties, i.e. the soil water characteristics and the unsaturated hydraulic conductivity, were proposed.

The model given by Brooks and Corey [10] was one of the earliest. Nowadays the most popularly used is a parametric model, in which van Genuchten introduced a class of functions that is continuously differentiable and applicable to a broader range of soil types [37]. The nonlinear unsaturated hydraulic properties, $q(h)$ and $K(q)$ are described by normalised water content function:

$$\Theta(h_s) = \frac{\theta - \theta_r}{\theta_s - \theta_r} = \begin{cases} [1 + (\alpha_G |h_s|)^{n_G}]^{-m_G} & \text{for } h_s \leq 0 \\ 1 & \text{for } h_s > 0 \end{cases} \quad (5)$$

Kool and Parker [22] modified the parametric model of van Genuchten to account for hysteresis and air entrapment. However, in the studies on significance of hysteresis in predicting solute transport in the near-surface region [24] a minor effect of hysteresis on pollutant transport in the considered systems was noticed. In the case of macroscopic structures, such as fractures or macropores, other models are discussed, e.g. two domain approaches considering macropore flow [19] or capillary flow [29].

The formulations of mass balance equations for the species in porous media can be classified depending on ongoing phenomena, assumed simplifications or considered case. The main tendencies in modelling solute transport in porous media are usually due to saturation (full or partial saturation), sorption processes ongoing in the system, wide range of pore water velocities distributions, geometrical system (one- or dimensional multidimensional models), etc.

Obviously, the saturation problem is consequently incorporated into the mass balance equations of the species assuming full saturation or partial saturation (constant or time-dependent); the examples of monographs were given above.

A quite simple formulation for describing pollutant transport of a non-reactive chemical species is presented in [23], assuming there are no sorption processes on the soil particles in one-dimensional case in the unsaturated zone:

$$\frac{\partial(\theta \cdot c)}{\partial t} = \frac{\partial}{\partial x} \left\{ D\theta \frac{\partial c}{\partial x} - qc \right\} \quad (6)$$

Assuming sorption processes with the lack of mass transfer resistances at the liquid-solid phase interface (so-called „dynamic local equilibrium assumption”), the sorbed concentration is algebraically related to the solution concentration, e.g. if the sorption process is described by linear isotherm, then:

$$s = K_s \cdot c \quad (7)$$

One-dimensional solute transport equation, assuming linear sorption isotherm, for the soil system as a whole (for transient fluid flow) is given by [38]:

$$\frac{\partial(\theta Rc)}{\partial t} = \frac{\partial}{\partial x} \left(\theta D \frac{\partial c}{\partial x} - qc \right) - \theta k_d c \quad (8)$$

$$k_d = k_l + \frac{\rho_s k_s K_s}{\theta} \quad (9)$$

while the retardation factor R is defined as:

$$R = 1 + \frac{\rho_s K_s}{\theta} \quad (10)$$

The model of pollutant migration assuming linear sorption isotherm was proposed in paper [44], while nonlinear sorption isotherms were considered for contaminant transport in packed soil column in [18]. The review of merits and disadvantages of the approach presented above showed that its use is limited to the clearly defined systems [14].

Taking into account the mass transfer resistances at the liquid-solid phase interface, the sorption rate, J_a , from the solution to the sorbed phase, assuming the linear sorption isotherm, is given by [38]:

$$J_a = \alpha_s \rho_s (K_s c - s) \quad (11)$$

One-dimensional model with one-site sorption kinetics includes the mass balance for the species for solution and solid phase, which becomes respectively [38]:

$$\frac{\partial(\theta c)}{\partial t} = \frac{\partial}{\partial x} \left(\theta D \frac{\partial c}{\partial x} - qc \right) - \alpha_s \rho_s (K_s c - s) - \theta k_l c \quad (12)$$

$$\frac{\partial s}{\partial t} = \alpha_s (K_s c - s) - k_s s \quad (13)$$

The model with one-site sorption kinetics (nonlinear sorption isotherms) most accurately described the pesticide transport in soils [31].

Two-Site sorption Model (also called Equilibrium / Kinetic Sorption Model) presumes that sorption or exchange sites in soils can be classified into two fractions: one fraction (Type-1) on which mass transfer resistances due to sorption can be neglected, and another fraction (Type-2) on which sorption kinetics is considered to be rate limiting [26, 38]. This approach is usually used to describe the transport of solutes that interacts with a solid phase composed of such different constituents as soil minerals, organic matter and various oxides.

Sorption onto Type-1 sites (assumed to be at „dynamic equilibrium”) is given by [38]:

$$\frac{\partial s_1}{\partial t} = f_{TS} K_s \frac{\partial c}{\partial t} \quad (14)$$

By using a linear sorption isotherm the mass balance equation for Type-2 sites is set as:

$$\frac{\partial s_2}{\partial t} = \alpha_s [(1 - f_{TS}) K_s c - s_2] - k_{s2} s_2 \quad (15)$$

where: subscripts „1” and „2” refer to the Type-1 and Type-2 sorption sites, respectively. The mass balance equation for the species for the system as a whole can be given by the following formulation:

$$\frac{\partial(c\theta)}{\partial t} + \rho \frac{\partial(s_1 + s_2)}{\partial t} = \frac{\partial}{\partial x} \left(\theta D \frac{\partial c}{\partial x} - qc \right) - \theta k_l c - \rho_s k_{s1} s_1 - \rho_s k_{s2} s_2 \quad (16)$$

The last two equations represent the complete Two-Site Model [38].

The prediction of migration of organic compounds (e.g. herbicide) in soil assuming the nonlinear sorption isotherms (Freundlich type) for both sorption sites for the steady-state flow is presented in work [15]. The results of the Two-Site Model validations show that for most solutes, although much simpler, the model neglecting the mass transfer resistances due to sorption, is quite satisfactory for prediction of concentration profiles [7].

In [9] three types of sorption kinetics are used to describe the transport of pesticides in non-structured arable soils, tested under field conditions. Gaston and Locke proposed a model for one-dimensional solute transport, with steady-state flow, for non-reactive system, in which sorption occurs at more than one site type, characterised by different sorption kinetics [15]:

$$\frac{\partial c}{\partial t} + \left(\frac{\rho_s}{\theta} \right) \sum_{j=1}^J \frac{\partial s_j}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} \right) - V \left(\frac{\partial c}{\partial z} \right) \quad (17)$$

A host of models was introduced to describe solute transport in soils that exhibit exceedingly wide distributions in pore water velocities.

The example of such approach is Two-Region Model (Mobile/Immobile Zone Model) [12, 39] in which the overall process rate is thought to be limited by the rate at which solutes are transported by diffusion to the exchange sites. This conceptualisation leads to models that partition soil water into mobile (flowing) and stagnant (immobile or non-flowing) regions. This approach in effect assumes that the pore-water distribution is bimodal: convective-dispersive transport is confined to a fraction of the liquid – filled pores only, while the remained pores have stagnant water (e.g. dead-end pore water, intra-aggregate water, thin liquid films around particles). In models of this type, solute exchange between the two liquid phase is usually considered to be a first order rate process. This model was proposed especially for aggregated or fractured media.

In such formulation of the problem, convective-dispersive transport is confined to a mobile liquid region (subscript „m”) while the presence of solute in an immobile region (subscript „im”) depends on liquid diffusion from the mobile to immobile liquid. The solid phase is also partitioned, in this case into a fraction f_{TR} that corresponds to the mobile fluid, and another fraction $(1-f_{TR})$ that corresponds to the immobile liquid. Sorption in the inter- and intra-aggregate regions of the soil is usually described with the use of linear sorption isotherms. Solute exchange between the mobile and immobile liquid regions is approximated by the expression:

$$J_{TR} = \alpha_s (c_m - c_{im}) \quad (18)$$

The transient-flow, one-dimensional, Two-Region transport Model with degradation consists of the following equations, for each of regions respectively [38]:

$$\frac{\partial(\theta_m c_m)}{\partial t} + f_{TR} \cdot \rho_s \frac{\partial s_m}{\partial t} = \frac{\partial}{\partial x} \left(\theta_m D_m \frac{\partial c_m}{\partial x} - q c_m \right) - J_{TR} - \theta_m k_{im} c_m - f_{TR} \rho_s K_s k_{sm} s_m \quad (19)$$

$$\frac{\partial(\theta_{im} c_{im})}{\partial t} + (1 - f_{TR}) \rho_s \frac{\partial s_{im}}{\partial t} = J_{TR} - \theta_{im} k_{im} c_{im} - (1 - f_{TR}) \rho_s k_{sim} s_{im} \quad (20)$$

Although mobile-immobile models are successful in describing solute transport in soil columns [15], they suffer from the fact that the model is operating on many fitted parameters that change as a function of experimental conditions [32].

Skopp et al. introduced a Dual Porosity Model for solute transport in soils whereby both regions are mobile and solute exchange occurs between the regions [34]. More recently a Dual Porosity Model was presented which accounts for both advective and diffusive exchanges of the solute under non-steady-state flow conditions [16]. This conceptualisation refers to the situation that soil often exhibits a variety of small-scale heterogeneity such as cracks, macropores and voids that permeate and separate the matrix or inter-aggregate pore regions. The consequences are wide variations in fluid velocity generated by heterogeneous void space within an averaging volume. The Dual Porosity Model approach consists of the introduction of a liquid pressure and mean velocity for each of the pore size groupings. Continuum equations of fluid and solute mass conservation are written separately for each pore size class; inter-region advective and diffusive exchange terms provide for the interaction between groupings.

One-dimensional, incompressible flow with negligible density effects due to concentration gradients, solute transport in each region is described in the form of equations [32]:

$$\frac{\partial(\theta_{p1}c_{p1})}{\partial t} + \frac{\partial(f_{DP}P_s s_{p1})}{\partial t} = \frac{\partial}{\partial x} \left(D_{p1}\theta_{p1} \frac{\partial c_{p1}}{\partial x} - V_{p1}\theta_{p1}c_{p1} \right) - \Gamma_{ex} \quad (21)$$

$$\frac{\partial(\theta_{p1}c_{p1})}{\partial t} + \frac{\partial(f_{DP}P_s s_{p1})}{\partial t} = \frac{\partial}{\partial x} \left(D_{p1}\theta_{p1} \frac{\partial c_{p1}}{\partial x} - V_{p1}\theta_{p1}c_{p1} \right) - \Gamma_{ex} \quad (22)$$

The subscripts „1” represent the macropore or inter-aggregate pore region, while subscripts „2” represent the soil matrix or intra-aggregate pore region. The net solute exchange rate Γ_{ex} comprises both advective and dispersive transfers.

The expanded Dual Porosity concept [17] uses three pore regions to describe water and solute transport under variably saturated conditions. This model partitions the soil into two mobile regions that represent the soil matrix and macropores. Exchange of solutes between pore groups is governed by advective and diffusive exchange coefficients between the three regions.

Since the mobility of pollutants in soil depends on complex physical, chemical and biological processes, a black-box approach basing on a multi-compartmental model is frequently employed, especially for describing radionuclide migration in soils.

In this approach the soil is split into a series of N horizontal layers (compartments) which are connected by downward transport rates of the radionuclide [13, 21]. Additionally, to modelling one-dimensional transport of radionuclide in porous medium, constant water content and linear sorption isotherm on the grains of the layer are assumed.

Kirchner suggested that the previously used serial Compartmental Model implicitly assumed convection-dominated flow and replaced it by a model with backflow for diffusion-controlled transport [20]. A compartmental representation of the above is given in form (subscript „ i ” refers to the considered i^{th} layer):

$$\frac{dc_1(t)}{dt} = -[\lambda + k_{1,2}]c_1(t) + k_{2,1}c_2(t) \quad (23)$$

$$\frac{dc_i(t)}{dt} = -[\lambda + k_{i,i+1} + k_{i,i-1}]c_i(t) + k_{i-1,i}c_{i-1}(t) + k_{i+1,i}c_{i+1}(t) \quad i = 2, \dots, N \quad (24)$$

The above equations correspond to situation where the downward transfer rates represent both convective and diffusive transport processes while the upward transfer rates are due to diffusion only.

However a number of conditions must be met so that the Compartment Model is a valid model of radionuclides in soil, e.g. the number of compartments should be set to a specific value, which is determined by the physical flow conditions in the studied soil. Because of the various limitations discussed in paper [20], every Compartmental Model should be used for predictions of long-term behaviour of radionuclides in the soil only after careful validation.

Contamination of groundwater resources due to spills or leakage of nonaqueous-phase organic liquids (NAPL) is of great environmental concern due to the hazardous nature of many constituent chemicals: fuels and mixed solvent wastes. Models of the movement of such materials in soils and groundwater must account for convective and dispersive transport and mass partitioning of multiple species in aqueous, gaseous, nonaqueous liquid and solid phases [5, 45].

The Multicomponent Model for a multi-ion system, incorporating the two retention mechanisms, ion exchange and specific sorption, into the convective-dispersion transport equation (for heavy metal ion „ i ”) is presented in [33]. The result of competitive adsorption column experiments of Cd and Zn are discussed and a mathematical model termed Competitive Dynamic Adsorption Model (CDAM) to predict the solute concentration in the multi-solute system is presented in [8] model of filtration through a fully saturated porous medium with an interaction between the solid matrix and liquid, in multi-species system is investigated in [36].

There exist different approaches to mass transfer modelling in granular media due to the geometrical system. One-dimensional models for migration of solute in porous systems are frequently encountered in describing pollutants migration in soil, many papers were discussed in the previous paragraphs, e.g.: [15, 20, 23, 32, 33, 36, 38]. One-dimensional models are often applied to the systems where the precise description of e.g. sorption terms or pores' water distribution is the main aim of the approach and these processes are rate limiting for the whole mass transfer. The simplification to the 1-D problem is also justified when there is no mass transport in the „horizontal” directions.

Multidimensional contaminant transport models have several advantages over one-dimensional models. First of all, multidimensional models can account for concentration gradients and contaminant transport in directions perpendicular to the groundwater flow, which can significantly contribute in mass transfer processes in grain layers. Therefore the anisotropy, frequently encountered in many natural processes, can be taken into account. The multidimensional models can more easily provide the experimental verification of the model by direct fitting of available experimental data (even from *in situ* „field” systems) and such models can account for a variety of boundary conditions as well as contaminant source geometries.

There were several approaches to multidimensional modelling of mass transport in grain layer, e.g [43]. The implementations of different numerical techniques for modelling pollutant migration are examined in [10, 30, 44].

Wroński et al. proposed a three-dimensional model of pollutant migration in fully saturated porous medium with additionally immobilisation of contaminant on sorptive agglomerates [41].

MODEL OF THE MIGRATION AND IMMOBILISATION
OF POLLUTANTS IN GRANULAR LAYER

Due to complex phenomena undergoing within the grain layer (e.g. soil), the solution of such a problem requires taking into account a number of simplifications. The following assumptions are made: the granular layer is described by a porous medium model (the velocity and pressure distributions are expressed by Darcy's law), particular bed is made of particles of an average diameter d_p , fate of a single pollutant is considered, concentration of the chemical compound, which penetrate the layer, is low enough to assume that mass transfer does not disturb the hydrodynamics of the water flow, pollutants can be reversibly sorbed onto the grains which make up the layer.

According to the listed assumptions, the general mass balance equations describing migration of the substance in a porous three-dimensional space were set up [41]. Anisotropy of the system and Cartesian orthotropy in a pseudohomogeneous porous layer is also assumed. The differential mass balance for solute in liquid has the following formulation [1, 2]:

$$\frac{\partial(c\theta)}{\partial t} + \vec{U} \nabla(\theta \cdot c) = \nabla(D\theta \nabla c) - \frac{(1-\varepsilon) \cdot \theta \cdot a'}{\varepsilon} \cdot J_{sor} - R_{liq} \theta \quad (25)$$

The differential mass balance for solute on the grains of the layer is given by the equation:

$$\frac{\partial c_s}{\partial t} = \frac{\theta \cdot a'}{\varepsilon} J_{sor} - \frac{\theta \cdot a'}{\varepsilon} R_{sol} \quad (26)$$

For the constant soil saturation (water content $\theta = const$) and diffusion coefficients ($D_{ii} = const.$), the equations (25) and (26) will take the form, respectively:

$$\begin{aligned} & \theta \frac{\partial c}{\partial t} + U_x \theta \frac{\partial c}{\partial x} + U_y \theta \frac{\partial c}{\partial y} + U_z \theta \frac{\partial c}{\partial z} = \\ & = \theta \cdot D_{xx} \frac{\partial^2 c}{\partial x^2} + \theta \cdot D_{yy} \frac{\partial^2 c}{\partial y^2} + \theta \cdot D_{zz} \frac{\partial^2 c}{\partial z^2} - \frac{(1-\varepsilon) \cdot \theta \cdot a'}{\varepsilon} \cdot J_{sor} - R_{liq} \cdot \theta \end{aligned} \quad (27)$$

$$\frac{\partial c_s}{\partial t} = \frac{\theta \cdot a'}{\varepsilon} J_{sor} - \frac{\theta \cdot a'}{\varepsilon} R_{sol} \quad (28)$$

The symbols R_{liq} and R_{sol} in the differential mass balances of a component mean mass sources of a contaminant in the liquid and solid phase, respectively. These terms represent the rate of disappearance of the pollutant due to chemical reaction or, on the contrary, appearance for example due to dissolution of the precipitated, hardly soluble salts, present in the deposit. The reaction in liquid phase R_{liq} refers to volume unit of liquid, while the reaction on the grains of the layer, R_{sol} , refers to the surface unit of wetted solid phase.

The solute flux, J_{sor} , describes a mass transfer rate (referred to a unit of wetted surface) from the solution to the solid phase due to adsorption (or desorption), and can be expressed in many forms, depending on the considered sorption isotherm in the system.

The proposed set of equations (25), (26) (or (27), (28) for constant water content) is the basic formulation and it can be modified, depending on the case considered, without introducing any meaningful changes in the fundamental model structure. For example, different initial and boundary conditions such as: surface precipitation of pollutant, inhomogeneous initial contamination of the layer etc., can be assumed, as well as, the proper sorption or reaction kinetics ought to be considered.

While conducting investigation work, there occurred a lot of problems which can be described by adaptations of this formulation: the leaking storage tanks, waste disposals or radioactive disposals propagation (point sources), atmospheric deposition of radioactive contaminants (surface sources), agriculture treatment with pesticides, herbicides or contaminated fertilisers etc.

The issue is treated as a general problem of mass transfer in such a system, however, also considering the practical technology of decontamination. The method consists in introducing the sorptive agglomerates into the polluted medium, where they efficiently adsorb the contaminants. After the proper time of incubation the sorbents can be removed from the layer enabling the permanent removal of pollutants. The basic model of pollutant migration presented above was adapted due to the considered sorptive technology of heavy metals removal. Therefore, additionally, the negative macroscopic mass sources, here in the form of sorptive bodies or sorptive agglomerates, immersed in the porous layer, were taken into account. The situation can refer to sorptive agglomerates appropriately inserted to the medium (due to decontamination) or natural agglomerates occurring in real systems.

The following assumptions were set up: agglomerates of an average d_a size containing a sorptive material are distributed regularly in the bed (preliminary assumption), the chemical compounds are „irreversibly” adsorbed on the agglomerates, up to a certain level of their saturation, full saturation of the bed is maintained. Such conditions follow the applied sorptive decontamination technology operating specification and are commonly assumed in the soil science researches.

In order to generalise the problem analysis the obtained model equations were transposed to a dimensionless form. The properly defined dimensionless parameters possess the physical sense corresponding to complex phenomena and actually constitute the process similarity criteria. This allows to discuss the effects of the variations within the wide range of the basic dimensionless parameters [3, 42]. Introducing the appropriately defined parameters and dimensionless variables yields to the following general model equations:

1. For a contaminant in the liquid phase:

$$\begin{aligned} \frac{\partial C}{\partial Fo} + Pe_x \frac{\partial C}{\partial X} + Pe_y \frac{\partial C}{\partial Y} + Pe_z \frac{\partial C}{\partial Z} = \\ = \frac{\partial}{\partial X} \left(D^{0_x} \frac{\partial C}{\partial X} \right) + \frac{\partial}{\partial Y} \left(D^{0_y} \frac{\partial C}{\partial Y} \right) + \frac{\partial}{\partial Z} \left(D^{0_z} \frac{\partial C}{\partial Z} \right) - \frac{6(1-\varepsilon)}{\varepsilon} Bi \cdot (C - C_s) - R_{liq}^0 \end{aligned} \quad (28)$$

In the case of a chemical reaction the mass source term will include the Dämkhöler number:

$$R_{liq}^0 = Da \cdot C \quad (29)$$

2. For a contaminant sorbed on the grains of the layer:

$$\frac{\partial C_s}{\partial Fo} = \frac{6}{K} Bi \cdot (C - C_s) \quad (30)$$

Two different models were considered [4, 40] depending on the mass transfer resistances occurring in the continuous and in the solid phase, referring to the real systems encountered in the decontamination technology.

Model I describes a system, where the effect of diffusion and adsorption within a sorptive agglomerate on mass transfer is negligible. This type of system may occur when the zeolithes are of a small size. In the case of dominant mass transfer resistance in the continuous phase of a convective type, it is possible to neglect the internal mass transfer resistances within agglomerate. The effective mass flux, determining the rate of mass transfer of pollutant from the liquid to agglomerate, can be expressed with the use of effective overall mass transfer coefficient (describing both mass transfer from the liquid to agglomerate as well as diffusion of substance within the pores of agglomerate and sorption on agglomerate):

3. The flux at the agglomerate's sublayer „envelope” surface, Model I:

$$\bar{J}(\Gamma_s) = Bi_a \cdot C(\Gamma_s) \cdot \left(\frac{d_p}{d_a} \right) = D^{0_n} \left(\frac{\partial C}{\partial N} \right)_{\Gamma_s} \quad (31)$$

Model II is a more general formulation as it considers the successive stages of mass transfer in the system. This model should be considered when a significant or decisive effect of mass transfer within the agglomerate (due to internal diffusion in agglomerate pores) to the whole mass transport resistances appears. This situation could be accompanied by a relatively weak influence of convection on the mass transfer effectiveness, as cases of small linear velocities of water flow across the layer (e.g. as a result of the atmospheric precipitation) or no convection at all. Decisive influence of mass transfer resistances within agglomerate to the whole mass transfer resistances could also appear for agglomerates of a relatively big size.

4a. The mass transfer within zeolithes is described by a diffusion of adsorbate molecules to the porous structure of an adsorbent [11]. Balance for a contaminant diffusing within and adsorbed on the agglomerate pores, Model II:

$$\frac{\partial C_{ag}}{\partial Fo} \cdot \left(\frac{d_a}{d_p} \right)^2 = D^{0_{ag}} \left(\frac{\partial^2 C_{ag}}{\partial R^2} + \frac{2}{R} \cdot \frac{\partial C_{ag}}{\partial R} \right) - Bi_{ag} \cdot \left(C_{ag} - \frac{C_{sag}}{K_{ag}} \right) \quad (32)$$

4b. Condition at the agglomerate's surface, Model II:

$$\bar{J}(\Gamma_a) = D^{0_n} \left(\frac{\partial C}{\partial N} \right)_{\Gamma_a} \cdot \left(\frac{d_a}{d_p} \right) = D^{0_a} \left(\frac{\partial C_{ag}}{\partial R} \right)_{\Gamma_a} \quad (33)$$

For the subsequent case (type of soil, type of contaminant, type of sorbent etc.) it is necessary to determine the transport, equilibrium and kinetic parameters, here entering the dimensionless numbers. The parameters, such as e.g.: D_{it} , K_{ag} , K , have a precisely rigorous physical meaning and should be determined in independent procedures. The coefficients k_{of} , k_s and k_{ag} , which enter the dimensionless Biot numbers appearing in the model would be rather difficult to direct determination and should be treated as process model parameters.

VERIFICATION OF THE MODEL

Verification of both operational models was provided, following the assumption of the regular distribution of agglomerates in the layer. Therefore, modelling was limited to a

computational space cell (limited by the planes of symmetry), being representative for the whole layer and following the assumptions listed previously.

For the numerical solution of the problem a program FIDAP v.8.00 offered by Fluent Inc., which contains a numerical implementation of the finite element method, has been applied. A relative error lower than 10^{-5} for each variable has been assumed as a convergence criteria for a solution.

Verification of Model I was provided basing on the experiments for the removal of lead from middle quartz sand and was conducted with the use of zeolithes formed in agglomerates of 5 mm diameter. In the considered experiments the medium was characterised by the following parameters: $K = 1,75$ [dm^3/kg], $K_{\text{ag}} = 2400$ [dm^3/kg], $D_{\text{sand}} = 3,58 \cdot 10^{-10}$ [m^2/s], $D_{\text{agglom}} = 8,3 \cdot 10^{-11}$ [m^2/s], $\varepsilon = 0,234$ [-]. The calculations were provided for different mass percentage of agglomerates in the system, according to experimental *pot tests*. The estimated values of process parameters represented by the proper Biot numbers took the values: $\text{Bi} = 3,1 \cdot 10^{-2}$ (refers to the rate of contaminant sorption on the grains of the layer) and $\text{Bi}_a = 1,3 \cdot 10^{-4}$ (refers to the rate of mass transfer from the liquid to agglomerate, expressed by effective mass transfer coefficient). The values of process parameters coefficients were obtained: $k_s = 1,1 \cdot 10^{-7}$ [m/s] and $k_{\text{ef}} = 2,2 \cdot 10^{-11}$ [m/s], respectively.

The data obtained from the experimental tests were determined in the pseudo-equilibrium conditions, after 5 months of incubation. Results of the experimental investigations as well as numerical calculations are shown in Table 1.

Table 1. Medium values of the amount of immobilised heavy metal on the zeolith, verification of Model I

Series	% (mass) of zeolithes in the system	Experimental data of % Pb immobilised on zeolith	Calculated mean value of % Pb immobilised on zeolith
P2	20%	68.0	99.9 *
P3	5%	27.2	23.1
P4	2%	8.8	8.9

Remark: *A bigger divergence for the high concentration of zeolithes is probably caused by randomness of the distribution of the agglomerates in porous medium. Therefore, the problem of the influence of distribution of negative mass sources (agglomerates) on the mass transport appeared, is shortly discussed below.

Experimental verification of Model II was provided basing on the experiments for the removal of lead from river alluvial soil with the use of sorptive agglomerates (zeolith 4A, 5 mm diameter). In the considered experiments the medium was characterised by the following parameters: $K_{\text{alluvial}} = 27$ [dm^3/kg], $K_{\text{ag}} = 2640$ [dm^3/kg], $D_{\text{sand}} = 4,49 \cdot 10^{-10}$ [m^2/s], $D_{\text{agglom}} = 8,3 \cdot 10^{-11}$ [m^2/s], $\varepsilon = 0,342$ [-]. The calculations were performed for different mass percentage of agglomerates in the system and for different time of incubation. The evaluated values of process parameters represented by the proper Biot numbers took the values: $\text{Bi} = 1,56 \cdot 10^2$ (refers to the rate of contaminant sorption on the grains of the layer) and $\text{Bi}_{\text{ag}} = 6,5 \cdot 10^7$ (refers to the rate of adsorption of pollutant on agglomerate). The values

of process parameters coefficients were obtained: $k_s = 3,33 \cdot 10^{-3}$ [m/s] and $k_{ag} = 1,12 \cdot 10^{-6}$ [m/s] ($k'_{ag} = 1,0 \cdot 10^3$), respectively.

The results of the experimental investigations as well as numerical calculations are given in Table 2.

Table 2. Medium values of the amount of immobilised heavy metal on the zeolith, verification of Model II

% zeolithes [% mass.]	Experimental data Percentage of Pb immobilised on zeolith m_z/m_{opb} [%]	Calculated values, Model II Percentage of Pb immobilised on zeolith m_z/m_{opb} [%]	Period of incubation [days]
5	7.1	5.9	43
5	8.8	8.5	71
5	9.6	12.2	140
10	12.7	10.9	43
10	14.8	15.3	71
10	15.8	20.0	99
10	18.5	25.1	140
15	15.1	16.4	43
15	19.3	23.2	71
15	28.0	35.2	140
20	19.5	22.1	43
20	25.9	31.1	71
20	35.3	45.0	140

Both dimensionless formulations of the models operate on properly defined dimensionless Biot numbers, being process parameters of the models. The differences in the definitions of the particular dimensionless Biot numbers revealed in the obtained values of these parameters.

The obtained calculations results validate functional effectiveness of the suggested method and its numerical implementation to anticipate migration and immobilisation of the contaminants within a porous layer in different conditions (Model I and Model II).

The geometry of the real systems, including the porous media structure, the source configuration and nonlinear sorption and/or chemical reaction on grains of the layer can be characterised by strongly non-uniform distributions. The presence of such „heterogeneities” in the medium greatly complicates a model analysis of mass and momentum transfer. The possible approach to solving such problem consists in following a strictly physical description of the process by the proper meso- or micro-scale equations. The problem of heterogeneity is then represented by the deviations from the regular system, assuming in a first step a quasi-regular distribution of mass sources.

The visible difference of results for bigger values of percentage of zeolithes in the layer is probably caused by casual (i.e. irregular) distribution of agglomerates in porous body. This effect is highlighted for a bigger percentage of agglomerates in medium.

Desorption of a component from the grains of the layer is a positive mass source uniformly distributed in the porous medium, while the sorptive agglomerates (negative mass sources) are distributed randomly regularly or irregularly (which occurs in the real systems) in the layer. The preliminary discussion analysis of the influence of irregular distribution of the point mass sources was presented in [1, 2]. In order to highlight the dominant problem of the effect of irregularity of negative sources distribution on the mass transport as the main goal, the mass point character of mass sources was analysed. Even a simplified analysis of the above presented problem indicates a significant influence of irregularities of mass sources (negative or positive) distribution on mass transfer, which gives a general idea about the considered issue. The estimation of the influence of distribution of negative (or positive) mass sources on mass transfer in the system would enable to provide more general model of the substance migration in the granular layer for different problems (e.g. point sources of radioactive deposits).

SUMMARY AND CONCLUSIONS

There are several approaches to modelling pollutant migration in granular media (e.g. soil) formulated to follow the certain purposes (e.g. the detailed sorption kinetics description). However, in practical problems, where we often deal with the only roughly recognised media, the application of the expanded formulations of mass transfer is often complicated. These models often suffer from the fact that they operate on many fitted parameters that change as a function of experimental conditions.

Therefore in several cases it seems to be beneficial to use the quite simple models of substance migration, although taking into account the subsequent processes of mass transfer. Therefore general model of pollutant migration in granular layer with additionally negative mass sources in the form of sorptive agglomerates was formulated. The effects of sorption of the contaminant on the grains of the layer, chemical reaction in the liquid and on the solid phase as well as the possible partial saturation of the layer by the liquid were considered. The general model was adapted to describe the examined decontamination technology and two operational models were differentiated due to the dominant mass transfer resistances in the system. The formulated equations were transposed into dimensionless form, which enabled to discuss the effects of their variations within the wide range of the basic dimensionless parameters that constitute the process similarity criteria. The experimental verifications of Model I and Model II were provided which validated the functional effectiveness of the suggested model and its numerical implementation under different conditions. The problem of influence of irregular distribution of negative mass sources (sorptive agglomerates) on mass transport in the granular layer was noticed.

Keeping in mind the assumed simplifications it is possible to estimate the pollutant's migration in granular medium for the practical purposes of decontamination technology. Main advantage and profit of the proposed model results from the possibility of approximate estimation of the mass transfer processes, using the constant values of Biot numbers, being process parameters characteristic for the considered media and model. Therefore it is possible to evaluate the concentration profiles of contaminant for different conditions and time. It gives the chance of practical application of proposed method.

SYMBOLS

- a' – specific area of considered granular medium e.g. soil or sewage sludge (defined as area of solid per volume of solid phase), [m²/m³];
 a_{ag} – specific area of agglomerate (area of agglomerate per volume of the whole agglomerate), [m²/m³];
 $Bi = k_s \cdot d_p / D_0$ – the Biot number determining mass transfer from the grains of the layer to the liquid filling the pores, [-];
 $Bi_a = k_{ef} \cdot d_a / D_0$ – the Biot number determining mass transfer from the liquid filling the pores of the layer to agglomerate, [-];
 $Bi_{ag} = k'_{ag} \cdot d_a^2 / D_0$ – the Biot number determining mass transfer from the liquid filling the agglomerate pores to solid phase of agglomerate, [-];
 c – eqns. (25) ÷ (33): concentration of contaminant in the liquid, [mol/m³];
 c – eqns. (1) ÷ (24): volume averaged solution concentration, [kg/m³];
 $C = c/c_0$ – dimensionless concentration of a contaminant in the liquid filling the bed pores, [-];
 c_{ag} – concentration of a contaminant in the agglomerate pores, [mol/m³];
 $C_{ag} = c_{ag}/c_0$ – dimensionless concentration of a contaminant in the liquid filling up the agglomerate pores, [-];
 $C_h(\theta) = d\theta/dh_s(\theta)$ – the specific soil water capacity, [kg/ms²];
 c_{im} – concentration in immobile fraction of the liquid, [kg/m³];
 c_m – concentration in mobile fraction of the liquid, [kg/m³];
 c_{p1} – resident solute concentration referred to volume of water in macropore pore region, [kg/m³];
 c_{p2} – resident solute concentration referred to volume of water in micropore pore region, [kg/m³];
 c_s – concentration of a contaminant adsorbed on the grains of the layer (e.g. sludge or soil), [mol/m³];
 $C_s = c_s/c_{s0}$ – dimensionless concentration of a contaminant adsorbed on the particles of the layer, [-];
 c_{sag} – concentration of a contaminant in agglomerate, [mol/m³];
 $C_{sag} = c_{sag}/c_0$ – dimensionless concentration of a contaminant in agglomerate, [-];
 c_{s0} – initial concentration of a contaminant adsorbed on the soil grains, $c_{s0} = c_0 \cdot K$, [mol/m³];
 c_0 – initial concentration of a contaminant in the liquid filling up the pores of the layer, [mol/m³];
 D – diffusion/dispersion coefficient, [m²/s];
 d_a – average diameter of agglomerate, [m];
 $Da = k \cdot d_p^2 / D_0$ – dimensionless Damköhler number, [-];
 D_{ag} – effective intraparticle diffusion coefficient (in liquid filling up the pores of agglomerate), [m²/s];
 D_{ii} – effective diffusion coefficient in liquid filling up the pores of the grain (the i-th coordinate), [m²/s];
 D_m – diffusion coefficient of the mobile zone [m²/s];
 d_p – average diameter of the grains of the layer (soil, sludge etc.), [m];
 D_{p1} – longitudinal dispersion coefficient for macropore pore region, [m²/s];
 D_{p2} – longitudinal dispersion coefficient for micropore pore region, [m²/s];

- D_0 – molecular diffusion coefficient, [m²/s];
 $D_{ag}^0 = D_{ag}/D_0$ – dimensionless intraparticle diffusion coefficient (in liquid filling up the pores of agglomerate), [-];
 $D_i^0 = D_{ii}/D_0$ – dimensionless diffusion coefficient in liquid filling up the pores of the grain layer, [-];
 f_{DP} – mass fraction of the soil that equilibrates with the solution in region 1, [kg/kg];
 $Fr_0 = (D_0 \cdot t) / d_p^2$ – Fourier number, [-];
 f_{TR} – fraction of solid phase that equilibrates instantaneously with the mobile fluid, [-];
 f_{TS} – fraction of exchange sites assumed to be at equilibrium in Two Site sorption model, [-];
 h_s – matric potential, [height of water column, (Pa)];
 J – mass flux, [mol/(m²·s)];
 J – dimensionless mass flux, [-];
 J_{sor} – mass flux due to sorption, the rate of reversible sorption of a contaminant on the grains of the layer, [mol/(m²·s)];
 J_{TR} – the transfer rate of pollutant due to diffusion-like exchange between the mobile and stagnant liquid, [kg/m³·s];
 k_{ag} – mass transfer coefficient (adsorption on agglomerates), [m/s];
 K_{ag} – equilibrium constant of the linear adsorption of pollutant on the zeolith, [-];
 $k'_{ag} = k_{ag} \cdot a_{ag} / \varepsilon_{ag}$ – modified mass transfer coefficient of adsorption on agglomerates, [m/s·m²/m³];
 k_d – total (or effective) degradation constant, [1/s];
 k_{ef} – effective mass transfer coefficient, [m/s];
 K_f – permeability of the porous medium, [m²];
 K_h – hydraulic conductivity, [m/s];
 k_{ij} – transport rate coefficient from soil layer i to j , [1/s];
 k_1 – first-order decay coefficient for degradation from the liquid phase, [1/s];
 k_{lim} – the immobile liquid phase degradation coefficient, [1/s];
 k_{liq} – chemical reaction rate constant in the liquid, [1/s];
 k_{lm} – the mobile liquid phase degradation coefficient, [1/s];
 k_s – eqn. (1)÷(24): the first-order sorbed phase degradation coefficient, [1/s];
 k_s – eqn. (25)÷(33): mass transfer coefficient of desorption of pollutant from the grains of the layer (e.g. soil), linear isotherm, [m/s];
 K_s – distribution coefficient, [kg/m³];
 k_{sim} – the first-order sorbed phase degradation coefficient for the immobile region, [1/s];
 k_{sm} – the first-order sorbed phase degradation coefficient for the mobile region, [1/s];
 k_{s1} – the first-order sorbed phase degradation coefficient on Type-1 sites, [1/s];
 k_{s2} – the first-order sorbed phase degradation coefficient on Type-2 sites, [1/s];
 m_G – positive fitting parameter, [-];
 n_G – positive fitting parameter, [-];
 p – pressure [Pa];
 $Pe_i = U_i d_p / D_0 = (U_i / U_{0i}) \cdot (U_{0i} \cdot d_p / D_0)$ – Péclet number, [-];
 q – the superficial velocity, the volumetric water flux density, [m/s];
 r – radial coordinate (in the pores of agglomerate), [m];
 $R = r/d_a$ – dimensionless radial coordinate, [-];
 R' – retardation factor, [-];

- R_{liq} – mass source, the rate of contaminant decay or appearance in the liquid, [mol/($m^3 \times s$)];
 $R_{liq}^0 = R_{liq} \cdot d_p^2 / D_0 \cdot c_0$ – dimensionless rate of contaminant disappearance or in the liquid, [-];
 R_{sol} – mass source, the rate of contaminant disappearance in solid phase due to chemical reaction, [mol/($m^2 \cdot s$)];
 s – sorbed concentration, [kg/kg];
 s_{p1} – adsorbed mass of solute per unit of soil mass that equilibrates with the solution of macropore pore region, [kg/kg];
 s_{p2} – adsorbed mass of solute per unit of soil mass that equilibrates with the solution of micropore pore region, [kg/kg];
 S_w – source/sink term (mainly due to root uptake of the water), [m^3/m^3s];
 s_1 – sorbed concentration on the Type-1 sorption sites, [kg/kg];
 s_2 – sorbed concentration on the Type-2 sorption sites, [kg/kg];
 t – time, [s];
 U_i – liquid velocity in the pores of the layer in the i -th direction, [m/s];
 U_{0i} – superficial liquid velocity in the i -th direction, [m/s];
 $V = q/\theta$ – the average pore water velocity, [m/s];
 V_{p1} – pore water velocity for macropore pore region, [m/s];
 V_{p2} – pore water velocity for micropore pore region, [m/s];
 x, y, z – coordinates, [m];
 X, Y, Z – dimensionless coordinate along the i -coordinate, $X = x/d_p, Y = y/d_p, Z = z/d_p$ [-].

GREEK SYMBOLS

- α_G – positive fitting parameter, [$m \cdot s^2/kg$];
 α_s – first-order kinetic rate coefficient, [1/s];
 α_{TR} – model-specific first-order mass transfer coefficient describing the rate of transfer between the mobile and immobile liquid phases, [1/s];
 ε – grain layer (e.g. sludge or soil) porosity, [-];
 ε_{ag} – agglomerate porosity, [-];
 Γ_{ex} – the net solute exchange rate per unit soil volume per unit time; [kg/m^3s];
 Γ_s – notation of a shell-formed surface across the agglomerate ($\delta_{shell} = (3 \div 5) \cdot d_p$);
 λ – the radioactive nuclide decay constant [1/s];
 μ_l – liquid viscosity, [$N/m^2 \cdot s$];
 θ – volumetric water content, [m^3/m^3];
 Θ – normalised water content, [-];
 θ_{im} – the volumetric immobile water content, [m^3/m^3];
 θ_m – the volumetric mobile water content, [m^3/m^3];
 θ_{p1} – macropore pore region volumetric water content, [m^3/m^3];
 θ_{p2} – micropore pore region volumetric water content, [m^3/m^3];
 θ_r – the residual volumetric water content, [m^3/m^3];
 θ_s – the saturated volumetric water content, [m^3/m^3];
 ρ – liquid density, [kg/m^3];
 ρ_s – soil bulk density, [kg/m^3].

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