

Simplified Mathematical Model of Conservative Pollutant Propagation in Ground Water Stream Including Adsorption Process

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Abstract

In the first part of this article, a mathematical model of conservative and passive pollutant propagation in one-dimensional flow of ground water (including advection and adsorption processes) has been presented. Basing on laboratory studies of pollution concentrations on a model for measuring adsorption and adopting the numerical solution for this mathematical model, adsorption parameters k_1 and n were also calculated (for non-linear function describing this process). In the second part, taking advantage of the calculated values of these parameters of adsorption, empirical relationships subjecting these adsorption parameters on both those characterising an aquiferous layer (competent diameter d_{10} , spatial ground porosity p) and ground water flow (water level or pressure line slope of ground water) were worked out. At the same time, the values of pollutant concentration reductions as a result of adsorption both from parameters characterising ground medium (competent diameter d_{10} , spatial ground porosity p), ground water flow (pressure line slope I) and estimated adsorption parameters (k_1, n) have also been worked out.

At the end of this article basing on the empirical equations for adsorption parameter values, the calculated values of pollutant concentrations have also been calculated and compared with the measured pollutant concentrations on a physical model.

1. Introduction

The main purpose of this article is determination of the relationships between ground adsorption capacity in ground water flow and competent diameters d_{10} and pressure line slopes of ground water. Ground adsorption capacity is defined as a pollutant quantity in flowing ground water, which can be adsorbed on ground grains in an aquiferous layer. Ground adsorption capacity has been expressed by empirical relationships in which occur adsorption parameters k_1 and n .

The range of this article is the following:

- formulation of mathematical pollutant propagation and adsorption model taking into account processes of advection and longitudinal dispersion,

- formulation and verification on a physical model of the adopted numerical model describing the adsorption process,
- definition of empirical relationships of adsorption parameters (k_1 , n) both from parameters characterising ground medium (competent diameter d_{10} , spatial porosity p) and slope I of water level or pressure line of ground water.

Such empirical relationships have not occurred in research by other authors so far.

Values of adsorption parameters have been defined in relation to laboratory or field research (Barovic 1979, Boochs et al. 1977, Gupta and Greenkorn 1974, Miller and Weber 1984, van Genuchten et al. 1974, Kleczkowski 1984, Hassanizadeh et al. 1990, Aniszewski 1998). For experimental definitions of adsorption parameters other research-workers used mainly indicator measurements, among others fluorescein, radioactive or neutron indicators (for example fluorescein, chemical component ions, radioisotope substances, brines or pesticides).

Values of adsorption parameters defined by various authors are related to:

- various mathematical descriptions of the adsorption process depending on research methods,
- various scales of research (laboratory or field),
- various types and shapes of laboratory columns or research carried out in one or many test wells,
- various Darcy velocities and kinds of ground media,
- various kinds of indicators (various chemical constitutions and concentration values) and measurement procedures,
- various measuring instruments and their measurement accuracy.

Differences in values of defined adsorption parameters are relatively considerable (in the range of three orders of magnitude). It should also be noticed, that adsorption parameters have been defined based on research with one kind of ground medium and one Darcy velocity of ground water. It could thus be difficult to use them at the same time for other ground kinds (ground diameters) and Darcy velocities (water levels or pressure line slopes of ground water).

The empirical relationships, determined by the author based on laboratory research and presented in this article, have a general meaning.

Pollutants of a conservative character occur increasingly in ground waters in practical cases (chlorides, heavy metals or toxic compounds).

Thus, rhodamine has been used as a conservative indicator in laboratory research carried out by the author on a physical model for adsorption measurement.

Before presentation of the mathematical pollutant propagation and adsorption model in a ground water stream, an explanation of the conservative and passive character of flowing pollutants is presented.

Advection of pollutants in the main direction of ground water flow is treated as a physical process, which consists in the change of concentration values, whereas, longitudinal and transverse dispersion processes in ground water are treated as physical processes, which consist in a change in concentration values caused by liquid element motions and pollutant concentration gradients in clear ground areas.

In the presented mathematical model of propagation, conservative and passive kinds of pollutants have been taken into account. Assuming also, that the aquiferous layer is homogeneous, the process of molecular diffusion has been neglected (Weinberger and Mandel 1973). This process occurs mostly in natural ground media.

The passive kind of pollutants is treated as such which have approximately the same density and viscosity as ground water.

To describe the propagation of conservative and passive pollutants and sorption in a ground water stream, the well-known advection-diffusion equation, resulting from transport continuity has been taken into account (Ogata 1970, Bear 1972):

$$\begin{aligned} \frac{\partial C}{\partial t} + v_x \frac{\partial C}{\partial x} + v_y \frac{\partial C}{\partial y} + v_z \frac{\partial C}{\partial z} = \\ = \frac{\partial}{\partial x} \left(D_x \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_y \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left(D_z \frac{\partial C}{\partial z} \right) - g_1 \end{aligned} \quad (1)$$

where:

- C – pollutant concentration in ground water,
- v_x, v_y, v_z – components of Darcy velocity,
- D_x, D_y, D_z – components of mechanical dispersion coefficient,
- t – time,
- g_1 – term generally describing the reversible physical sorption process.

The right side of the equation (1) is related to pollutant dispersion for anisotropic ground media in the three main propagation directions x , y and z assumed. Assuming, that axes of coordinate system (x, y, z) coincide with mixing axes, on the right side of equation (1) only three main components of dispersion tensor D_x , D_y and D_z exist (Ogata 1970, Małoszewski 1978).

The term (g_1) describes the reversible physical sorption process in general, treated in further analysis as adsorption (g_2) and desorption (g_3) processes.

2. Mathematical Equation of Pollutant Propagation and Adsorption

Taking into account the homogeneous ground medium, the constant values of mechanical dispersion D_x , D_y and D_z that do not depend on coordinate position,

were assumed in equation (2).

Thus, the right side of equation (1) can be written in the form of equation (2) (Bear 1979, Małoszewski 1978):

$$\frac{\partial C}{\partial t} + v_x \frac{\partial C}{\partial x} + v_y \frac{\partial C}{\partial y} + v_z \frac{\partial C}{\partial z} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} - g_1 \quad (2)$$

Assuming one-dimensional flow of ground water along the axis of the column with the ground (x), Darcy velocities v_y and v_z have been ignored ($v_y = v_z = 0$). Thus, the equation (2) can be written as:

$$\frac{\partial C}{\partial t} + v_x \frac{\partial C}{\partial x} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} - g_1 \quad (3)$$

Basing on the continuous influx of pollutants into a ground water stream and ignoring the pollutant frontal zone, the term of longitudinal dispersion ($D_x \partial^2 C / \partial x^2$) has been ignored as being considerably smaller (in the range of two or three orders of magnitude), than the term of advection ($v_x \partial C / \partial x$) along the main direction of ground-water flow (Ogata 1970, Barovic 1979, Boochs et al. 1977, Gupta and Greenkorn 1974).

The pollutant frontal zone is defined as the distance in which concentration reduction occurs as a result of longitudinal dispersion in the direction of ground water flow. The length of the frontal zone is situated symmetrically towards the front of the water flow with Darcy velocity, hence, the indicator concentration in place of the front flow amounts, according to theoretical calculations, to half of the concentration in cross-section, which is situated behind the frontal zone (Ogata 1970, Booch et al. 1977, Barovic 1979).

Negligence in the mathematical model (5) pollutant frontal zone generated by longitudinal dispersion, resulted from its negligibly small length, which was proved basing on earlier laboratory research carried out on a physical model (Fig. 3). During laboratory research a rhodamine as indicator was used in greater concentration than that causing adsorption capacity depletion of used grounds in the column. Measured on ground model length of pollutant frontal zone ca. 0.04 m in cross-section $x = 1.20$ m for ground about $d_{10} = 0.26$ mm in diameter and Darcy velocity $v_x \cong 1.10 \times 10^{-5}$ m s⁻¹ has been presented in Figure 1.

Neglecting this zone, displacement of the pollutant front with Darcy velocity has been assumed. Based on measured indicator concentration values in the length of the pollutant frontal zone (Fig. 1) the value of longitudinal dispersion coefficient D_x was calculated and amounted to ca. 0.25×10^{-9} m² s⁻¹. It proved the possibility of negligence of the longitudinal dispersion term ($D_x \partial^2 C / \partial x^2$) compared with the value of the advection term ($v_x \partial C / \partial x$) (Ogata 1970, Małoszewski 1978).

Distances on axis x presented in Figure 1 are presented in distorted scale taking into account the small length of frontal zone in relation to the length of

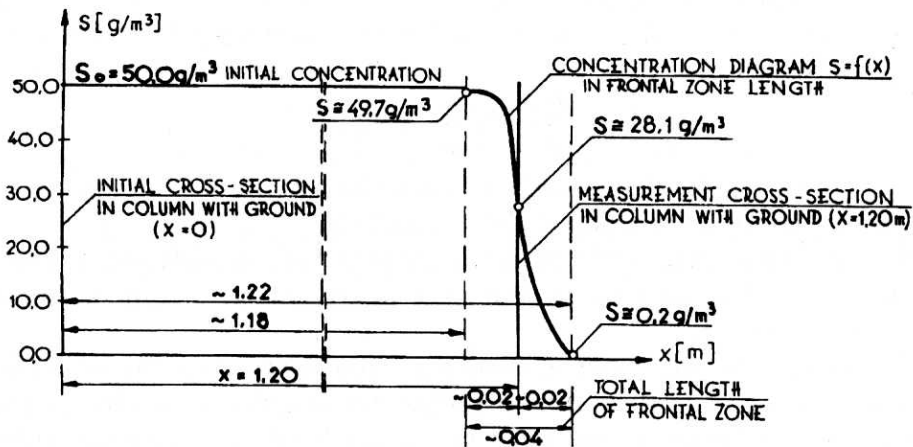


Fig. 1. Diagram of pollutant concentration relationship $C = f(x)$ in frontal zone

the column with ground. Based on laboratory research on ground model, it was defined that for smaller Darcy velocity $v = v_x/2 \cong 0.59 \times 10^{-5} \text{ m s}^{-1}$, the total length of frontal zone was also smaller and amounted in cross-section $x = 1.20 \text{ m}$ to ca. 0.022 m .

As a cause of small lengths of frontal zones were:

- small Darcy velocities of ground water ($1.18 \times 10^{-5} \leq v_x \leq 5.23 \times 10^{-4} \text{ ms}^{-1}$),
- small values of competent diameters ($0.26 \leq d_{10} \leq 1.16 \text{ mm}$).

Basing on experimental research carried out by other authors, for greater ground diameters and greater Darcy velocities of ground water, frontal zone lengths were also greater (Boochs et al. 1977, Barovic 1979, Macioszczyk and Szestakow 1984). Thus, the mathematical models of pollutant propagation presented in the literature took into account frontal zones and the influence of the longitudinal dispersion term ($D_x \partial^2 C / \partial x^2$).

So, taking into account the above remarks, the term of longitudinal dispersion has been neglected in further analysis ($v_x \partial C / \partial x \gg D_x \partial^2 C / \partial x^2$).

Thus, the equation (3) can be presented as:

$$\frac{\partial C}{\partial t} + v_x \frac{\partial C}{\partial x} = D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} - g_1 \quad (4)$$

Taking into account the relatively small diameter of the column with the ground and certain distance from the indicator influx to the initial cross-section ($x = 0$) in this column, full equalisation of pollutant concentration values in transverse (y) and (z) directions for all measuring cross-sections (Fig. 3) has been assumed.

Based on the above assumption, the dispersion terms ($D_y \partial^2 C / \partial y^2 = 0$) and ($D_z \partial^2 C / \partial z^2 = 0$) have also been neglected in the equation (4). Thus, the equation (4) can be written as:

$$\frac{\partial C}{\partial t} + v_x \frac{\partial C}{\partial x} = -g_1 \quad (5)$$

It should be noted, that the retardation process (as a result of adsorption) is taken into account as the $\partial C / \partial t$ term in the equation (5).

Before the presentation of a mathematical model of reversible sorption process in a ground medium, the notions of physical adsorption and desorption processes have been presented.

The adsorption process of pollutants in ground water can be explained as a physical process which consists in pollutant accumulation on the surface of particular ground grains as the result of van der Waals intermolecular adhesive forces. This type of adsorption is treated as a reversible process which causes certain reduction of the concentration values in ground water.

At the same time in the presented mathematical propagation model, the term representing the chemical adsorption process (so called chemisorption) has been neglected, taking into account the author's earlier research between used indicator and ground materials. Chemical adsorption exists in the case of chemical reactions between flowing pollutants in ground water and the surface of ground medium grains. This type of adsorption can be treated as an irreversible process.

The term g_1 in the equation (5) describing the reversible physical sorption process can be expressed as (Bear 1979, Miller and Weber 1984, van Genuchten et al. 1974):

$$g_1 = \frac{\rho(1-p)}{p} \frac{\partial S}{\partial t} \quad (6)$$

where:

- S – mass of sorbed solute pollutants (solid phase concentration) on the ground grains per unit mass of ground,
- ρ – solid phase density of ground medium treated as constant value for the assumed homogeneous ground,
- p – spatial porosity coefficient of ground medium treated also as constant value for the assumed homogeneous ground.

According to Miller and Weber (1984), van Genuchten et al. (1974), the $\partial S / \partial t$ expression consists of the following two terms which can be written as:

$$\frac{\partial S}{\partial t} = \frac{\partial S_a}{\partial t} - \frac{\partial S_d}{\partial t} = g_2 - g_3 \quad (7)$$

where:

- S_a – mass of adsorbed pollutant on the ground grains per unit mass of ground,
- S_d – mass of desorbed pollutant from the ground grains into ground water per unit mass of ground,
- $\partial S_a / \partial t = g_2$ – term determined by that part of pollutants adsorbed on the ground grains, which is subjected to adsorption process,
- $\partial S_d / \partial t = g_3$ – term determined by that part of pollutants desorbed from the ground grains into ground water, which is subjected to desorption process.

Following Boochs et al. (1977), Barovic (1979), Miller and Weber (1984), van Genuchten et al. (1974), the term describing the adsorption process (g_2) has been accepted as:

$$g_2 = k_1 \frac{P}{\rho(1-p)} C^n \quad (8)$$

and respectively, the term describing desorption process (g_3) as:

$$g_3 = k_2 S_d \quad (9)$$

where:

- k_1 – adsorption coefficient as the rate constant for the adsorption process,
- k_2 – desorption coefficient as the rate constant for the desorption process,
- n – constant index exponent of the non-linear adsorption process.

Thus, taking into account the above literature sorption models, the author also assumed the accurate non-linear shape of the function describing the physical adsorption process g_2 (related to liquid phase concentration) and linear function describing the physical desorption process g_3 (related to quantity of sorbed solute pollutants on the ground grains per unit mass of ground as solid phase concentration) according to (8) and (9).

Hence, the equation (7) can be written as:

$$\frac{\partial S}{\partial t} = g_2 - g_1 = k_1 \frac{P}{\rho(1-p)} C^n - k_2 S_d \quad (10)$$

The presented non-linear function describing the adsorption process (8) and linear relationship describing the desorption process (9) are recommended for a description of these processes taking into account the relatively substantial compatibility between the mathematical description of these and experimental research on adsorption and desorption processes in ground water. This compatibility has also

been confirmed by author based on experimental research defining adsorption parameters on a laboratory model for adsorption measurement (Aniszewski 1996, Aniszewski 1998).

Following Boochs et al. (1977), Barovic (1979), Miller and Weber (1984), van Genuchten et al. (1974), Kowal (1990), it can be said, that for continuous influx of indicator into ground water, the rate of the desorption process (g_3) can be neglected.

Thus, taking into account continuous influx of indicator during the author's research, the desorption process (g_3) as the equation (9) has been neglected in further calculations.

Taking into account this assumption concerning the neglecting of the desorption process, the equation (10) has been written as:

$$\frac{\partial S}{\partial t} = k_1 \frac{P}{\rho(1-p)} C^n = g_2 \quad (11)$$

and adequately, the equation (6) including the equation (11) can be written as:

$$g_1 = \frac{\rho(1-p)}{p} k_1 \frac{P}{\rho(1-p)} C^n = k_1 C^n \quad (12)$$

It should be noticed, that the equation (12) is related to one value of spatial ground porosity p . Hence, the equation (5) taking into account the equation (12) can be presented as:

$$\frac{\partial C}{\partial t} + v_x \frac{\partial C}{\partial x} = -k_1 C^n \quad (13)$$

In the further calculations this equation (13) has been taken into account as the one which simultaneously includes advection and adsorption processes. These processes occur and are dominated (with exception of longitudinal dispersion) during indicator propagation on a physical model for adsorption measurement for continuous influx of pollutants into a ground water stream.

Basing on laboratory research and using the equation (19), the adsorption parameters k_1 and n have been determined by the author of the article (Aniszewski 1998).

In order to present the considerable differences in values of adsorption parameters (k_1 , n), Table 1 (columns 4 and 5) give chosen values of adsorption parameters determined in earlier research by other authors and by the author of this article, based on the accepted mathematical description on the adsorption process according to (12). Values of adsorption parameters presented in Table 1 are related to a different kind of indicators (various chemical constitutions) of flowing pollutant but for similar values of: competent diameter d_{10} (spatial porosity p) of analysed grounds, slopes of pressure line of ground water, initial concentration of indicators used and cross-section in laboratory columns with ground. In column

(6) of Table 1, the author presented values of rhodamine concentrations (for an initial concentration of 50.0 g m^{-3}), based on the equation (19) and taking to this equation values of adsorption parameters determined by other authors mentioned in Table 1.

Table 1. Compilation of adsorption parameters (k_1 , n) based on both the author's research and other authors' experiments together with calculated concentration values according to (19)

No.	Author of research	Kind of indicator	Values of adsorption parameters		Values of concentration acc. to (19) [g m ⁻³]
			$k_1 \cdot 10^4$ [m ³⁽ⁿ⁻¹⁾ g ⁻⁽ⁿ⁻¹⁾ s ⁻¹]	$n \cdot 10^2$ [dimensionless]	
1	2	3	4	5	6
1	Boochs et al. (1977)	potassium nitrate ion KNO ₃ ⁻	0.172	13.81	32.57
2	Gupta and Greenkorn (1974)	potassium hydrogen phosphate ion KH ₂ PO ₄ ⁻	0.145	11.64	34.83
3	van Gnuchten et al. (1974)	pesticide	0.043	0.58	48.44
4	Hassanizadeh et al. (1990)	brine	0.116	6.13	40.23
5	Aniszewski (1998)	rhodamine B.	0.077	1.84	45.18

The great differences in values of both adsorption parameters and concentrations presented in Table 1 are the result of many factors mentioned in Chapter 1 of this article, but primarily from the various kinds of indicators used and their degree of dissociation.

3. Numerical Solution of Advection and Adsorption Equation for Defining Adsorption Parameters

The equation (13) can be solved analytically, but this makes it possible to determine concentration values only for times t treated as advection times $t = x/v_x$, ($x = v_x t$). Thus, the analytical solution of the equation (13) is limited only for the pollutant front in particular ground cross-sections. Thus, the author used the numerical solution of the equation (13), that permits determination of concentration values as coordinate function x for constant value t and as time function t for $x = \text{constant}$. Relationship $S = f(t)$ for constant cross-section x permits the taking into account of retardation of the adsorption process (Aniszewski 1998).

Following O'Brien (1988), the equation (13) has been solved by means of the well-known finite difference method (FDM). In this method, the examined continuous ground area is replaced by a discrete area which consists of nodes of the assumed calculation scheme grid (Aniszewski 1997 and Aniszewski 1998).

For numerical solution of the equation (13), the adequate boundary condition and the initial condition related to the horizontal indicator flow in column with ground have also been accepted.

– boundary condition:

$$C = C_0 \text{ for } x = 0 \text{ and for } 0 \leq t \leq \infty \quad (14)$$

and respectively,

– initial condition:

$$C = 0 \text{ for } t = 0 \text{ and for } 0 < x \leq \infty \quad (15)$$

The examined initial cross-section along column length ($x = 0$) is treated as the cross-section in a certain distance from indicator influx to column with ground where the full concentration equalisation has been accepted. In this initial cross-section, the initial concentration of indicator (C_0) has also been assumed taking into account the relatively small distance of this cross-section from the pointwise influx of indicator into column with ground (ca. 10 cm).

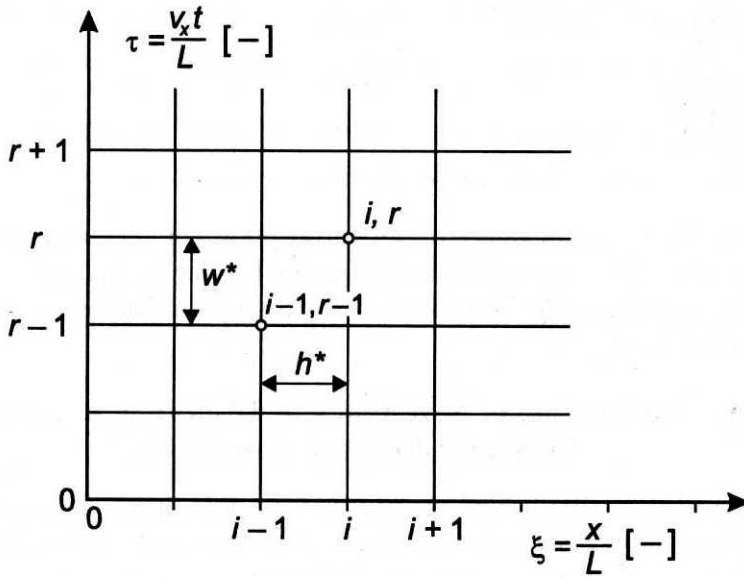


Fig. 2. Scheme of the assumed coordinate system for equation (19)

Taking into account notations and additional dimensionless parameters (Aniszewski 1997 and Aniszewski 1998) (Fig. 2):

$$\left. \begin{aligned} \frac{x}{L} &= \xi; & \frac{C}{C_0} &= C^* \\ \frac{v_x t}{L} &= \tau; & \frac{k_1 L C_0^{(n-1)}}{v_x} &= A_1 \end{aligned} \right\} \quad (16)$$

where:

- L - the examined length of column with ground ($L = 3.0$ m),
 C_0 - pollutant concentration in an initial cross-section ($x = 0$).

Hence, the equation (13) can be written in the dimensionless form:

$$\frac{\partial C^*}{\partial \tau} + \frac{\partial C^*}{\partial \xi} = -A_1(C^*)^n \quad (17)$$

Concentration derivatives of pollutants for the equation (13) have been approximated by means of reverse concentration difference, because of the known measured concentration values in the reverse nodes along the column length. The established calculation algorithm permits passing on to the next calculation cross-section automatically, where the new equation system will be contained so-called "free" terms expressed by the known values of the measured concentration values in the nodes of the reverse cross-section.

Using the finite-difference method and reverse differences related to directions (ξ) and (τ), the form of the equation (17) can be written as (Fig. 2):

$$\frac{C_{i,r}^* - C_{i-1,r-1}^*}{w^*} + \frac{C_{i,r}^* - C_{i-1,r-1}^*}{h^*} = -A_1(C_{i,r}^*)^n \quad (18)$$

In further analysis the asterisk symbol for concentration values has been neglected ($C^* = C$).

The unknown value of the concentration in the $C_{i,r}$ node about coordinates (i, r) has been determined from transformation of equation (18) to the final form:

$$b C_{i,r} + A_1 C_{i,r}^n = (B + h_1) C_{i-1,r-1} \quad (19)$$

also taking into account additional dimensionless simplifying assumptions:

$$\frac{1}{w^*} + \frac{1}{h^*} = b; \quad \frac{1}{w^*} = B; \quad \frac{1}{h^*} = h_1 \quad (20)$$

For the numerical solution of the equation (19), equations for the concentration values are obtained in which exists the only single non-linear unknown, the other unknowns being in linear form.

Hence, for solution of the equation (19), the simple iteration method has been assumed (as the main iteration) and additionally, the unknown non-linearity of concentration value has been solved by means of the "regula falsi" method (as the inside iteration, using the consecutive secants). Accepting the "implicit" scheme for the numerical solution of the non-linear equation (19) with the inside iteration, the boundary condition according to (14) and the initial condition according to (15) presented earlier have also been used (Krupowicz 1986 and Marciniak et al.

1992). In the numerical solution of equation (19) presented, adequate steps of the examined calculation scheme grid in directions (ξ) and (τ) as the assumed adsorption axis have also been accepted. The examined step of calculation scheme grid along the column with ground is related to the ratio of the cross-section distances in the column (at 0.12 m intervals) to the total measuring length of this column.

Hence, the dimensionless step of the calculation scheme grid along the column length can be written as:

$$\Delta\xi = h^* = \frac{x}{L} = \frac{0.12 \text{ m}}{3.0 \text{ m}} = 0.04 \quad (21)$$

whereas, time steps of the calculation scheme grid have been assumed in relation to the previously defined physical and hydraulic parameters on laboratory column with ground.

The value of maximum advection time (for $x = 0.12$ m distance) can be written for $d_{10} = 0.26$ mm and $I = 2.15\%$ as:

$$\Delta t_{\max} = \frac{x}{v_{x \min}} = \frac{0.12 \text{ m}}{1.18 \cdot 10^{-5} \text{ m/s}} \cong 10170 \text{ s (ca. 2.82 h)} \quad (22)$$

and the value of minimal advection time (for $x = 0.12$ distance) for $d_{10} = 1.16$ mm and $I = 10.76\%$ as:

$$\Delta t_{\min} = \frac{x}{v_{x \max}} = \frac{0.12 \text{ m}}{5.23 \cdot 10^{-4} \text{ m/s}} \cong 230 \text{ s (ca. 0.06 h)} \quad (23)$$

Hence, the dimensionless time step can be written as:

$$\left. \begin{aligned} \Delta\tau &= w^* = \frac{v_{x \min} \Delta t_{\max}}{L} = \frac{1.18 \cdot 10^{-5} \text{ m/s } 10170 \text{ s}}{3.0 \text{ m}} = \\ &= \frac{v_{x \min} \Delta t_{\max}}{L} = \frac{5.23 \cdot 10^{-4} \text{ m/s } 230 \text{ s}}{3.0 \text{ m}} \cong 0.04 \end{aligned} \right\} \quad (24)$$

The accepted steps of the calculation scheme grid for both the steps according to (21) and those according to (24) are bigger than maximal steps resulting from preservation of the convergence conditions of numerical solution of the equation (19) (Aniszewski 1998).

A description and the assumed numerical solution method has been given in detail in Aniszewski (1997) and Aniszewski (1998).

To make the numerical solution of the equation (19) easier, the calculation program "SORPCJA-1" (in Turbo Pascal language 6.0) has also been worked out.

4. Experimental Research to Determine Adsorption Parameters k_1 and n

To determine the values of adsorption parameters, experimental research has been carried out both with Darcy velocity (dynamic adsorption) and without Darcy

velocity (static adsorption) using various indicators (Barovic 1979, Boochs et al. 1977, Gupta and Greenkorn 1974, Kleczkowski 1984, Kowal 1990, Aniszewski 1998).

Values of adsorption parameters in flowing ground water are less due to flow of ground water, than parameters defined in lentic ground water. This is due to the fact, that in flowing ground water van der Waals intermolecular adhesive forces influencing adsorption process are less than analogical forces for lentic ground water.

This has also been verified for the chosen all ground kinds based on the author's earlier laboratory research in conditions of lentic ground water.

For example, the values of static adsorption parameters (using rhodamine) for a ground medium with a diameter of about $d_{10} = 0.26$ mm and spatial porosity $p = 32.5\%$ amount to $k_1 = 0.98 \cdot 10^{-5} [\text{m}^{3(m-1)}\text{g}^{-(n-1)}\text{s}^{-1}]$ and $n = 0.31 \cdot 10^{-1}$ whereas, in conditions of dynamic adsorption the average value $k_1 = 0.77 \cdot 10^{-5} [\text{m}^{3(m-1)}\text{g}^{-(n-1)}\text{s}^{-1}]$ and $n = 0.18 \cdot 10^{-1}$.

The remaining adsorption parameter values both static and dynamic adsorption are in the author's archive copy.

The author determined adsorption parameters for flowing ground water in relation to a physical model used in laboratory research (Fig. 3).

Based on the measured indicator concentrations on the physical model, the parameters of adsorption process (k_1, n) have been determined from the equation (19) (Aniszewski 1998).

A solution of rhodamine ($\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$) was used as the conservative indicator, which was also distinguished with a good solubility and density close to water, besides which, it did not react with the grounds applied in laboratory research.

The simplicity of using rhodamine as an indicator, resulted in the colorimetric indicator concentration measurement being used (colorimeter "Specol-11" together with feed amplifier for a filter about the length of a 472 nm transmitted wave).

In the laboratory research the seven kinds of ground media were used, diameters of which were in the range of average and coarse sands ($0.62 \leq d_{10} \leq 1.16$ mm) and the one ground kind in the range of fine sands ($d_{10} = 0.26$ mm). Values of ground competent diameters d_{10} used in laboratory research were also related to values of spatial porosity coefficients p , adequately for coarse sands in the range of $37.6 \leq p \leq 41.5\%$ and for fine sand $p = 32.5\%$ (Fig. 3). It should be noticed, that such wide ranges of diameters for sands can exist most often in the truly aquiferous layers of the saturated zone.

Samples of concentration defining of rhodamine solution were drawn in the 25 constant cross-sections of column with ground for advection times $t_c = x/v_x$. For visualisation of indicator solution flow in the laboratory model, the glass column was used, whose the fairly small diameter (ca. 6 cm) enabling quick equalisation

of indicator concentration from the pointwise influx of indicator into the column with ground to the initial cross-section.

The rhodamine solution was let in as continuous pointwise influx with an initial concentration of $C_0 = 50.0 \text{ g}\cdot\text{m}^{-3}$. In the initial cross-section, the indicator concentration as (C_0) has also been assumed taking into account the relatively short distance of this cross-section from pointwise influx (ca. 10 cm).

During the laboratory research five-times of pressure line slope of ground water (I) was changed for one kind of ground medium in the wide range of $2.15 \leq I \leq 10.76\%$. Total sample number of indicator concentration measurements amounted to ca. 2600.

The values of the remaining parameters characterising both ground water flow in column with ground during research and porosity of the chosen grounds were in the ranges:

- hydraulic conductivity $5.50 \cdot 10^{-4} \leq k \leq 4.86 \cdot 10^{-3} \text{ [m s}^{-1}\text{]}$,
- spatial porosity coefficient $32.5 \leq p \leq 41.5 \text{ [%]}$,
- Darcy velocity $1.18 \cdot 10^{-5} \leq v_x \leq 5.23 \cdot 10^{-4} \text{ [m s}^{-1}\text{]}$,
- discharge value $1.34 \cdot 10^{-7} \leq Q \leq 5.91 \cdot 10^{-6} \text{ [m}^3 \text{ s}^{-1}\text{]}$.

The precise digital values for hydraulic conductivity (k), spatial porosity (p) and competent diameter (d_{10}) have been presented in Table 2.

5. Elaboration of Empirical Research for Physical Adsorption Processes

Basing on the measured indicator concentration values and numerical solution of the equation (19), the parameters of the adsorption process (k_1, n) have been determined. In further analyses the results of laboratory measurements enabled elaboration of empirical relationships of the adsorption parameters from the values characterising both ground medium (d_{10}) and ground water flow (I).

In the first turn, the empirical relationship of k_1 from pressure line slopes I and competent diameters d_{10} and related to these diameters values of spatial porosity p and index exponents n were worked out.

This equation can be written in the exponential form:

$$k_1 = a_1 \exp[-b_1 I] \quad (25)$$

where:

$$\left. \begin{aligned} a_1 &= 0.2259 \cdot 10^{-4} d_{10} + 0.4214 \cdot 10^{-6} \\ b_1 &= 3.2629 d_{10} + 20.0337 \end{aligned} \right\} \quad (26)$$

The values of (d_{10}) diameters should be taken in [mm] and values of (I) pressure line slopes in [%].

The presented relationship of adsorption parameter k_1 from the pressure line of ground water (treated as output value) is of considerable practical meaning.

Very often disposing of pressure lines or water levels of ground water measured in a natural aquiferous layer, it is possible to determine values of adsorption parameters according to (25) without the necessity to calculate Darcy velocity and cross-section distance (advection time). In the equation (25) values of pressure lines of ground water are treated as measured output values similar to competent diameters and ground porosity values.

Practical application of the equations (25) and (26) is related to the numerical range of competent diameters ($0.26 \leq d_{10} \leq 1.16$ mm), spatial porosity ($3.25 \leq p \leq 41.5[\%]$) and adsorption exponents ($0.0031 \leq n \leq 0.0192$).

A diagram of the calculated and the equalised values of (k_1) parameters in relation to pressure line slopes of ground water I for three chosen competent diameters d_{10} , spatial porosity coefficients p and index exponents n is presented in Figure 4.

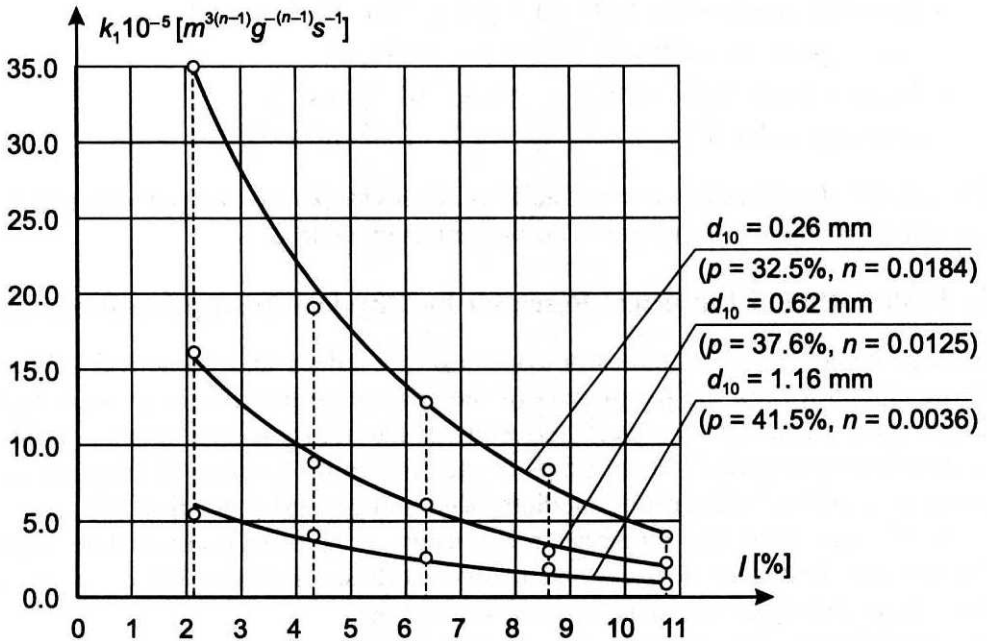


Fig. 4. Values of adsorption coefficients (k_1) in relation to pressure line slopes of ground water I , ground competent diameters d_{10} , spatial porosity coefficients p and index exponents n : \circ - the calculated values according to (19), - - - - the equalised values according to (25)

In the next turn, the empirical relationship of adsorption index exponents n from competent diameters d_{10} in the range of spatial porosity $32.5 \leq p \leq 41.5\%$ was worked out.

This experimental relationship can be written as:

$$n = b_2 d_{10} + c \quad (27)$$

where:

$$\left. \begin{aligned} b_2 &= -0.1672 \cdot 10^{-1} \\ c &= 1.0230 \end{aligned} \right\} \quad (28)$$

The values of (d_{10}) diameters should be taken in mm.

The diagram of the calculated and the equalised values of adsorption exponents (n) in relation to competent diameters d_{10} (spatial porosity coefficients p) is presented in Figure 5.

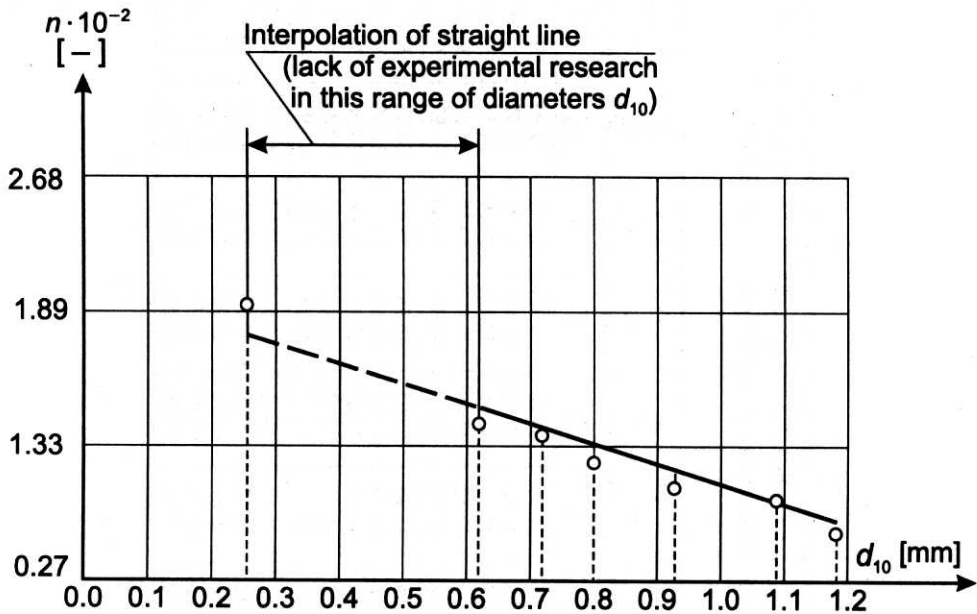


Fig. 5. Values of dimensionless constant index exponents of adsorption process (n) in relation to ground competent diameters d_{10} in the range of porosity coefficients ($32.5 \leq p \leq 41.5\%$): o – the calculated values according to (19), - - - the equalised values according to (27)

Spatial porosity p related to competent diameters (axis of abscissae) is changed in the range (Fig. 5):

d_{10} [mm]	0.26	0.62	0.71	0.80	0.92	1.08	1.16
p [%]	32.5	37.6	38.7	39.8	40.3	40.9	41.5

In the next turn of this analysis using the equalised values of adsorption parameters according to the equations (25), (26), (27) and (28), the verification of the indicator concentrations (C_c) according to (19) (as the calculated values) has been made for cross-sections in column with the ground and for the calculated advection times $t_c = x/v_x$. These calculated concentration values (C_c) have been compared with the measured concentration values (C_m) in the same cross-sections (Table 2).

Table 2. Compilation of the measured (C_m) and the calculated (C_c) indicator concentration values according to (19) for the three chosen ground competent diameters (d_{10}) and the examined pressure line slope of ground water (I) in the cross-sections along column with ground (k – hydraulic conductivity; p – spatial porosity coefficient)

No.	d_{10} [mm]	I [dimensionless]	$x_1 = 0.6$ m		$x_2 = 1.2$ m		$x_3 = 1.8$ m		$x_4 = 2.4$ m		$x_5 = 3.0$ m		
			C_m , [g m ⁻³]	C_c , [g m ⁻³]	C_m , [g m ⁻³]	C_c , [g m ⁻³]	C_m , [g m ⁻³]	C_c , [g m ⁻³]	C_m , [g m ⁻³]	C_c , [g m ⁻³]	C_m , [g m ⁻³]	C_c , [g m ⁻³]	C_m , [g m ⁻³]
1	2	3	45.87	45.18	41.61	40.20	37.30	35.17	32.95	30.11	28.58	25.01	
1	0.26 ($k \approx 5.50 \cdot 10^{-4}$ m s ⁻¹) ($p \approx 32.5\%$)	0.021538	46.00	46.09	41.86	42.06	37.68	37.99	33.46	33.88	29.22	29.75	
			46.25	46.19	42.39	42.26	38.48	38.29	34.54	34.29	30.58	30.27	30.27
			46.41	46.79	42.72	43.49	38.97	40.15	35.20	36.78	31.41	33.39	33.39
		0.107692	46.84	46.94	43.59	43.79	40.30	40.60	36.97	37.39	33.63	34.16	
2	0.62 ($k \approx 1.42 \cdot 10^{-3}$ m s ⁻¹) ($p \approx 37.6\%$)	0.021538	47.02	46.55	43.96	43.03	40.88	39.47	37.18	35.90	34.67	32.21	
			47.11	47.18	44.16	44.30	41.18	41.40	38.18	38.48	35.18	35.55	35.55
			47.36	47.27	44.65	44.47	41.93	41.66	39.20	38.83	36.45	36.00	36.00
		0.086153	47.52	47.74	45.00	45.42	42.43	43.09	39.86	40.74	37.30	38.39	
		0.107692	47.78	47.91	45.52	45.77	43.25	43.61	40.95	41.44	38.65	39.27	
3	1.16 ($k \approx 4.86 \cdot 10^{-3}$ m s ⁻¹) ($p \approx 41.5\%$)	0.021538	47.86	47.57	46.18	45.11	43.51	42.64	41.33	40.17	39.14	37.69	
			48.30	48.32	46.42	46.62	44.87	44.91	43.15	43.20	41.42	41.49	41.49
			48.36	48.46	46.69	46.91	45.02	45.35	43.35	43.35	41.67	42.32	42.32
		0.086153	48.57	48.65	47.15	47.28	45.71	45.92	44.27	44.54	42.82	43.17	
		0.107692	48.68	48.69	47.36	47.36	46.04	46.04	44.71	44.70	43.38	43.46	

As has been specified based on error analysis, the differences between the measured and the equalised concentration values (in relation to the measured concentration values) did not exceed 15%, which proves sufficient accuracy of equalisation method for defining adsorption parameters in the ground water flow conditions. The error values can also prove sufficient accuracy of the accepted mathematical description of physical adsorption process according to (12).

The author also presents relationships of indicator concentration reductions ΔC_a both from accepted parameters (d_{10} , I) and estimated adsorption parameters (k_1 , n).

The diagram of indicator concentration reductions ΔC_a from competent diameters d_{10} (spatial porosity coefficients p) for constant pressure line slope $I = 2.15\%$ is presented in Figure 6.

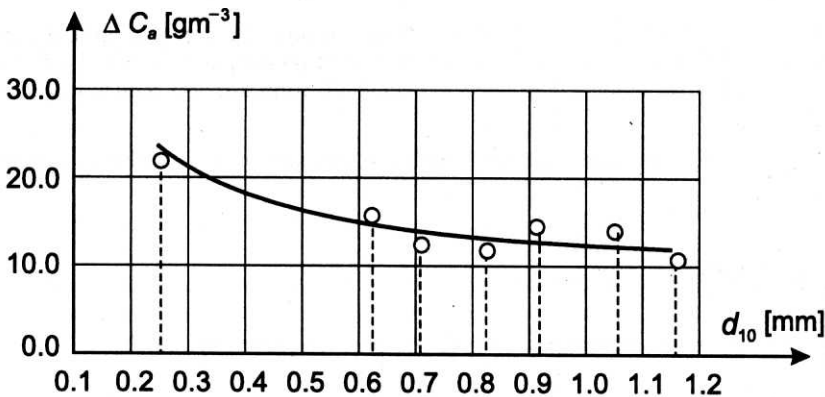


Fig. 6. Indicator concentration reduction ΔC_a from competent diameters d_{10} for pressure line slope of ground water $I = 2.15\%$: \circ – the measured concentration reduction values, — the equalised concentration reduction values

Basing on this diagram, can be found an increase of indicator concentration reduction as a result of adsorption for decreasing values of competent diameters d_{10} (spatial porosity p). This is caused by an increase in total surface of ground grains per volume of ground unit.

A diagram of indicator concentration reductions ΔC_a from pressure line slopes of ground water I for constant competent diameter $d_{10} = 0.26$ mm and spatial porosity coefficient $p = 32.5\%$ is presented in Figure 7.

Basing on this diagram, decrease of indicator concentration reduction as a result of adsorption for increasing values of pressure line slopes of ground water I can be found. This is caused by decrease, for increasing Darcy velocities, of van der Waals intermolecular adhesive forces resulting in an adsorption process.

The diagram of indicator concentration reductions ΔC_a from adsorption parameters k_1 for constant competent diameter $d_{10} = 0.26$ mm, spatial porosity coef-

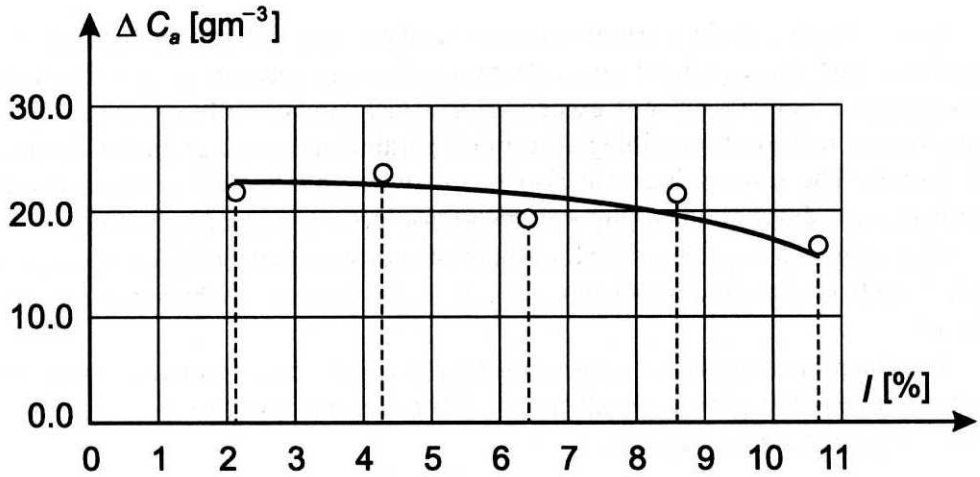


Fig. 7. Indicator concentration reduction ΔC_a from pressure line slopes of ground water I for constant competent diameter $d_{10} = 0.26$ and coefficient of porosity $p = 32.5\%$: \circ - the measured concentration reduction values, — - the equalised concentration reduction values

efficient $p = 32.5\%$ and for constant index exponent $n = 0.0184$ is presented in Figure 8.

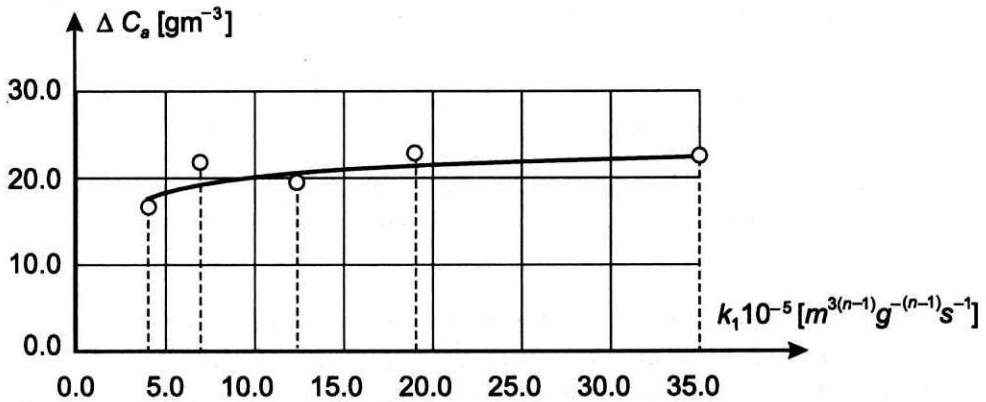


Fig. 8. Indicator concentration reduction ΔC_a from adsorption parameters k_1 for competent diameter $d_{10} = 0.26$, coefficient of porosity $p = 32.5\%$ and for constant index exponent $n = 0.0184$: \circ - the measured concentration reduction values, — - the equalised concentration reduction values

Basing on this diagram, can be found an increase of indicator concentration reduction for increasing values of adsorption parameters k_1 according to accepted by author mathematical adsorption model according to (12) and it also means increase of indicator concentration reduction for decreasing values of pressure line slopes of ground water I .

The author then worked out diagrams of calculated concentration values in the chosen cross-sections $C_c = f(x)$ according to (19) on physical model for the chosen time coordinates adequated to advection times $t_c = x/v_x$.

The example diagram of indicator concentration values in the chosen cross-sections on a physical model for time coordinate $t_c = L/v_x = 3.0 \text{ m}/1.18 \cdot 10^{-5} \text{ m s}^{-1} \cong 254420 \text{ s} \cong 70.7 \text{ h}$ (for $d_{10} = 0.26 \text{ mm} = \text{constant}$ and $I = 2.15\% = \text{constant}$) is presented in Figure 9.

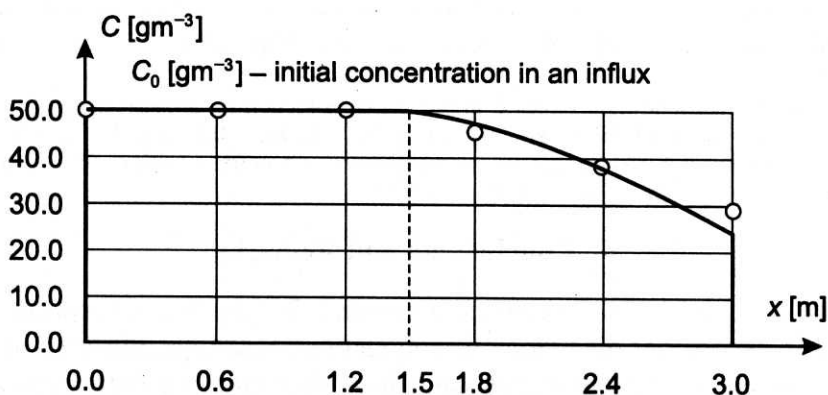


Fig. 9. Indicator concentration values C in the chosen cross-sections on a physical model for the chosen time coordinate $t_c = L/v_x = 3.0 \text{ m}/1.18 \cdot 10^{-5} \text{ m s}^{-1} \cong 254420 \text{ s} \cong 70.7$ ($d_{10} = 0.26 \text{ mm}$, $I = 2.15\%$): \circ – measured concentration values (C_m), — – calculated concentration values (C_c) according to (19)

Basing on this diagram, can be found that for time coordinate $t_c = 254420 \text{ s}$ (70.7 h), the initial concentration $C_0 = 50.0 \text{ g m}^{-3}$ occurs in column with ground in 1.5 m distance. In the distance between 1.5 m and 3.0 m indicator concentration is less than initial concentration C_0 as a result of the adsorption process.

At the end of the laboratory research author also worked out in Figure 10 the diagram of indicator concentration values in the last cross-section on physical model ($x = L = 3.0 \text{ m}$) $C_c = f(t_c)$ according to (19) from time coordinates t_c (in range $L/v_x \leq t_c \leq 2L/v_x$).

Basing on this diagram, can be found that maximum reduction of indicator concentrations for time coordinate $t_c = L/v_x$ occurs as a result of the adsorption process.

For increase of time coordinates $t_c > L/v_x$, the concentration values gradually increase up to the value of initial concentration C_0 . For time coordinates $t_c \geq 2L/v_x$, concentration values such as initial concentration C_0 can already be treated as constant value (lack of adsorption process).

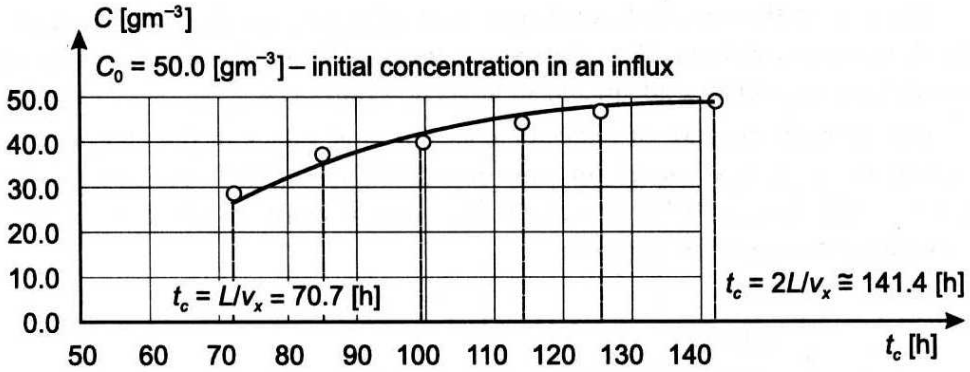


Fig. 10. Indicator concentration values C in the last cross-section on physical model ($x = L = 3.0$ m) from time coordinates t_c (in range $L/v_x \leq t_c \leq 2L/v_x$), ($d_{10} = 0.26$ mm, $I = 2.15\%$): \circ - the measured concentration values (C_m), - - the calculated concentration values (C_c) according to (19)

6. Conclusions and Remarks

Mathematical model and experimental research on physical adsorption process which were carried out on a laboratory model confirmed quantitative relationships between the adsorption parameters and those characterising both a ground medium (competent diameter d_{10}) and ground water flow (pressure line slope of ground water I) in the wide range of the examined sandy ground media. Both the model for adsorption measurement and the procedure of experimental research on this model took into account the accepted simplifying assumptions for both the propagation model and for the physical adsorption process.

In the opinion of the author, taking into account the lack of such practical relationships in literature so far, adsorption parameters (k_1 , n), depending on the values of (d_{10}) and (I) should be especially emphasized. In the next stage of laboratory research, the author intends to work out empirical relationships of adsorption parameters (k_1 , n) and pollutant concentration reductions (ΔC_a) also in relation to changeable values of ground spatial porosity p . The computer calculation program also enables practical numerical calculations of adsorption parameters based on the measured concentration values of flowing pollutants in the ground medium. The computer calculation program also enables more precise simulation of pollutant concentration fields compared with simulation based on pollutant propagation models without adsorption process, and at the same time enables better prognosis of quality water resources inflowing to ground water intakes.

Also of significant meaning in cases of calculations of protection zone borders for the influence of existing pollutant sources (industrial factories, waste material storages, sewage and sanitary deposit reservoirs from industrial and agricultural production) existing on protection zone sites of ground water intakes.

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