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**Using of experimental research  
for analysis of sorption term  
in groundwater contaminant  
transport equation**

# The final 2D-equation of advection-dispersion contaminant transport in ground medium

$$\frac{\partial C}{\partial t} \left( 1 + \frac{\rho}{m} \frac{\partial S}{\partial C} \right) + u_x \frac{\partial C}{\partial x} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} \quad (1)$$

$C$  – the solute concentration in flowing groundwater in aqueous phase (in the local equilibrium conditions),

$S$  – the mass of the solute species adsorbed on the grounds per unit bulk dry mass of the porous medium (in the local equilibrium conditions),

$u_x$  – the component of the average (real) seepage velocity in pore space along the x axis (as pore velocity),

$D_x$  – the component of the longitudinal dispersion coefficient along the x axis,

$D_y$  – the component of the transverse dispersion coefficient along the y axis,

$\rho$  – the bulk density of the porous medium ,

$m$  – the effective porosity of the porous medium,

$t$  – the co-ordinate of time,

$x, y$  – the co-ordinates of the assumed reference system.

# The basic simplified assumptions

- Leaving out of advection terms ( $u_y \partial C / \partial y = u_z \partial C / \partial z = 0$ ) for one – dimensional flow of groundwater in  $x$  direction ( $u_y = u_z = 0$ )
- Leaving out of transverse dispersion term ( $D_z \partial^2 C / \partial z^2 = 0$ ) in  $z$  direction for slotted contaminant outflow and initial concentration equalization in this direction
- Leaving out of molecular diffusion process due to low values of molecular diffusion coefficients ( $D_M$ ) in relation to values of dispersion rates ( $D_x$  and  $D_y$ )
- Leaving out of turbulent diffusion process ( $D_B$ ) for laminar groundwater flow in sandy ground medium (low graining)

# Description of the analysed kinetic sorption models

1) The first-order kinetic model (as the non-linear kinetic equation):

$$\frac{\partial S}{\partial t} = \frac{m}{\rho} \cdot k_1 \cdot C^N - k_2 \cdot S \quad (2)$$

$k_1, k_2$  – the rate constants of adsorption and desorption process,

$N$  – adsorption constant characterising geometric shape of adsorption isotherm (in the local equilibrium conditions).

2) The first-order kinetic model (as the linear kinetic equation  $N = 1$ ):

$$\frac{\partial S}{\partial t} = \frac{m}{\rho} \cdot k_1 \cdot C - k_2 \cdot S \quad (3)$$

For the local equilibrium-controlled state ( $\partial S/\partial t = 0$ ),  
the equation (2) can be written in the form:

$$S = \frac{k_1}{k_2} \cdot \frac{m}{\rho} \cdot C^N = K_2 \cdot C^N \quad (4)$$

where:  $\frac{k_1}{k_2} \cdot \frac{m}{\rho} = K_2$  is the constant non-linear adsorption parameter

and the equation (3) can be written in the form:

$$S = \frac{k_1}{k_2} \cdot \frac{m}{\rho} \cdot C = K_1 \cdot C \quad (5)$$

where:  $\frac{k_1}{k_2} \cdot \frac{m}{\rho} = K_1$  is the constant linear adsorption parameter

**For the great sorption rate this process is equilibrium-controlled one where concentration change in liquid phase ( $\partial C/\partial t$ ) is directly proportional to concentration change in solid phase ( $\partial S/\partial t$ )**

**So, it can be written relationship:**

$$\frac{\partial C}{\partial t} = \frac{\rho}{m} \cdot \frac{\partial S}{\partial t} \quad (6)$$

**and the non-linear kinetic equation (2) can be presented as :**

$$\frac{\partial C}{\partial t} = -k_1 \cdot C^N + k_2 \cdot a_0 \cdot S \quad (7)$$

**where:**

$$a_0 = \rho/m \quad (7a)$$

**Based on the own static "batch" experimental research (in the state of the final equilibrium), the mass balance of the moving contaminants (as adsorbate) can be written as:**

$$S = \frac{V \cdot (C_0 - C)}{m_0} \quad (8)$$

**where:**

**$V$  – the constant volume of examined contaminant solution with initial concentration  $C_0$ , used to inundate in laboratory research the ground samples of mass  $m_0$ ,**

**$m_0$  – the mass of the examined ground samples,**

**$C_0$  – the initial concentration of the examined contaminant solution.**

Using the previous equation (8) resulting from the own “batch” experimental research, the non-linear kinetic equation (7) can be written as:

$$\frac{\partial C}{\partial t} = -k_1 \cdot C^N + k_1 \cdot a_1^* \cdot (C_0 - C) \quad (9)$$

and respectively the linear kinetic equation (3) can be presented as:

$$\frac{\partial C}{\partial t} = -k_1 \cdot C + k_1 \cdot a_2^* \cdot (C_0 - C) \quad (10)$$

where:

$$\left. \begin{aligned} a_1 &= [(a_o \cdot V) / m_o] \\ a_2 &= [(1 / a_o) \cdot K_2] \\ a_3 &= [(1 / a_o) \cdot K_1] \end{aligned} \right\} \quad (10a)$$

$$\left. \begin{aligned} a_1^* &= a_1 \cdot a_2 = \frac{V}{m_o \cdot K_2} \\ a_2^* &= a_1 \cdot a_3 = \frac{V}{m_o \cdot K_1} \end{aligned} \right\} \quad (10b)$$



# Determination of the rate constant of adsorption ( $k_1$ ) for the non-linear kinetic equation (9)

Assuming exemplary number value of the constant Freundlich exponent ( $N = 2$ ) analytical solution of the non-linear kinetic equation (9) is in the form

$$C = \frac{B \cdot (A \cdot e^{k_1 \cdot t \cdot B} + 1) - a_1^* \cdot (A \cdot e^{k_1 \cdot t \cdot B} - 1)}{2 \cdot (A \cdot e^{k_1 \cdot t \cdot B} - 1)} \quad (11)$$

taking also into consideration the auxiliary expression:

$$\frac{-2 \cdot k_1 \cdot C_o - k_1 \cdot a_1^* - \sqrt{-\Delta}}{-2 \cdot k_1 \cdot C_o - k_1 \cdot a_1^* + \sqrt{-\Delta}} = A; \quad \sqrt{4 \cdot a_1^* \cdot C_o + a_1^{*2}} = B \quad (12)$$

where the discriminant (delta  $\Delta$ ) is:

$$\Delta = -4 \cdot k_1^2 \cdot a_1^* \cdot C_o - k_1^2 \cdot a_1^{*2}; \quad [\Delta < 0]$$

# Determination of the rate constant of adsorption ( $k_1$ ) for the linear kinetic equation (10)

Assuming number value of the constant Freundlich exponent ( $N = 1$ ) analytical solution of the linear kinetic equation (10) is in the form

$$C = C_0 \left[ \frac{e^{-k_1 \cdot t(1+a_2^*)} - a_2^*}{1 - a_2^*} \right] \quad (13)$$

Having the determined rate constant of adsorption ( $k_1$ ) from equations (11)-(12) and (13), the rate constants of desorption ( $k_2$ ) for the non-linear and linear model of sorption kinetics can be given, respectively as:

$$k_2 = \frac{k_1}{a_o \cdot K_2} = \frac{k_1 \cdot m}{K_2 \cdot \rho} \quad (14)$$

$$k_2 = \frac{k_1}{a_o \cdot K_1} = \frac{k_1 \cdot m}{K_1 \cdot \rho} \quad (15)$$

# Final conclusions

- 1) In the current literature lacks practical relationships between kinetics and statics of sorption process (models) which can be used in groundwater contaminant transport models (equations).
- 2) So, the attempts of practical connections (relationships) between the rate constants in non-linear and linear sorption kinetics models ( $k_1, k_2$ ) and the constant non-linear and linear isotherm parameters ( $K_1, K_2, N$ ) were presented in this analysis.
- 3) The presented attempts enable in practice to use of relatively simple "batch" experimental research (with immobile groundwater) instead of complex and long-lasting (expensive) laboratory or field research in order to obtain the so-called breakthrough curves (BTCs) required as transition ones in dynamic conditions (with mobile groundwater).

*Thank you for your attention*