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DETERMINATION OF TRANSPORT PARAMETERS OF SOILS AROUND SOLT

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Abstract

A complex labor investigation was performed to determine the adsorption properties of soils around Solt. After collection of samples firstly the soil type was determined as a pre-information of adsorption tests. Two type of experiment were performed to know the adsorption performance of soils: batch test and breakthrough curve test. In both investigation two type of soil (*SD a* sandy clayey silt, *SV a* sandy silty clay) *and two type of heavy metals (Mn and Zn) were investigated. In batch test the Langmuir and the Freundlich isotherms were used to determine the adsorption constants. According to our results the fitting of Freundlich isotherm was better for both soil, and the adsorption of Mn* ($K_{f,SD}$ = *2.28,* $K_{f,SV}$ = *1.74) was more intensive than Zn* ($K_{f,SD}$ = *1.27,* $K_{f,SV}$ = *0.84). After performance of static adsorption test, dynamic adsorption test, breakthrough curve test was also performed. The characteristic of adsorption was similar like in case of batch test. The value of distribution coefficient was higher in case of soil SD, and the adsorption was more intensive for Mn.*

Keywords: *heavy metals, batch test, breakthrough curve test, retardation factor*

1. Introduction

To perform a transport model input parameters are needed. From references, a lot of information can be found for data on typical soil types but this information will never result in an accurate transport model like models base on measured data.

There are two methods to determine transport parameters: the batch test and the breakthrough curve test. The first is a static investigation: uniform amount of soil samples are added to several vessels, then solutions with different known concentrations of investigated heavy metal are added to the solid phase. According to the aim of investigation the kinetics, the dynamics and the equilibrium of adsorption could be investigated. In case of adsorption equilibrium, the end of investigation is stabilization of concentration change in the solution. After analysis of solutions the performance of the adsorbent is evaluable. The parameter is resulted from the batch test is adsorption capacity (Zavvar Mousavi & Seyedi, 2011):

$$q = \frac{(C_0 - C)}{w} v \tag{1}$$

where C_0 and C are initial and final concentrations of the heavy metal [$mg \cdot L^{-1}$], V is volume of solution [L] and W is dry weight of adsorbent [g]. Equilibrium studies are conducted at a constant temperature to describe the relationship between adsorbed amount and equilibrium concentration of the investigated heavy metal in mathematical form. About the constant temperature conditions the curves of adsorption capacity in function of equilibrium concentration are called isotherms *(Figure 1)*. When there is a linear relationship between adsorbed amount of heavy metal and equilibrium concentration, it is called linear adsorption and is described by the following equation (Fetter, 1999):

$$q_e = K_d \cdot C \tag{2}$$

where q_e is mass of adsorbate on dry unit weight of soil [$mg \cdot g^{-1}$], C is the solute concentration in equilibrium with the mass of solute adsorbed onto the soil [$mg \cdot L^{-1}$] and K_d is distribution coefficient [$L \cdot g^{-1}$].

The common adsorption processes rarely can be expressed by linear adsorption (Kovács, 2004), in this situation, the Langmuir and the Freundlich isotherm equations are used to describe the equilibrium. The Freundlich isotherm can be preferred to describe the adsorption processes when it is happened as ion exchange, so an ion A on the surface of the adsorbent is changed to ion B from the soil solution *(Figure 1)*. With the increase of concentration, the number of exchanged ion B increases on the solid surface, which process is better followed by the continuously rising form of Freundlich isotherm (Freundlich, 1907). The Freundlich adsorption isotherm is defined as the amount of adsorbed substances per amount of adsorbent in solution at a constant temperature. It is written by the equation (Sparks, 2003):

$$q_e = K_F \cdot C^{\frac{1}{n}} \tag{3}$$

where q_e is mass of heavy metal adsorbed on unit amount [g] of adsorbent, C_e is the equilibrium heavy metal concentration in liquid phase [$mg \cdot L^{-1}$], K_F is the Freundlich constant [$L \cdot g^{-1}$] related to adsorption capacity and intensity of adsorption, and n is a correction factor.

The Langmuir isotherm (Langmuir, 1918) is more describe the situation when “empty” sorption places are filled *(Figure 1)*. There is 4 assumptions during use of the isotherm: (1) The adsorption happen on flat surface, where there is given number of adsorption sites and each can hold one molecule. Only monolayer coverage is permitted. (2) Adsorption is reversible. (3) There is no lateral movement of molecules on the adsorbent surface. (4) The binding places adsorption energy are equivalent to all sites, the surface is homogeneous, there is no interaction between molecules. In soils where heterogeneous surfaces are found these assumptions are invalid, so the Langmuir isotherm is more used for qualitative and descriptive purposes (Sparks, 2003). The equation of Langmuir isotherm is:

$$q_e = \frac{q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \tag{4}$$

where q_e is the adsorbed amount of adsorbate per unit mass of adsorbent [$mg \cdot g^{-1}$], C_e is the adsorbate concentration is in equilibrium ($mg \cdot L^{-1}$), q_{max} is the maximum adsorption capacity ($mg \cdot g^{-1}$), and K_L is the Langmuir equilibrium adsorption constant ($L \cdot mg^{-1}$). To evaluate the adsorption process when Langmuir isotherm is used a dimensionless constant was defined (Meroufel et al., 2013):

$$\boldsymbol{R_L = \frac{1}{1 + K_L \cdot C_0}} \tag{5}$$

where C_0 ($mg \cdot L^{-1}$) is the initial concentration and K_L ($L \cdot mg^{-1}$) is the Langmuir constant related to the energy of adsorption. The value of R_L can help to judge the favorability of adsorption process. When R_L is 0, the value of K_L is very large, the adsorption is too strong, also called irreversible. If value of R_L is between 0 and 1, means the standard case when the adsorption happens normally, the adsorption is favorable. When the value of R_L is equal to 1, the value of K_L is 0, this means that adsorption is linear. If the value of R_L is higher than 1, the K_L should be negative, in this case the adsorption is not favorable, it is desorption (Meroufel et al., 2013).

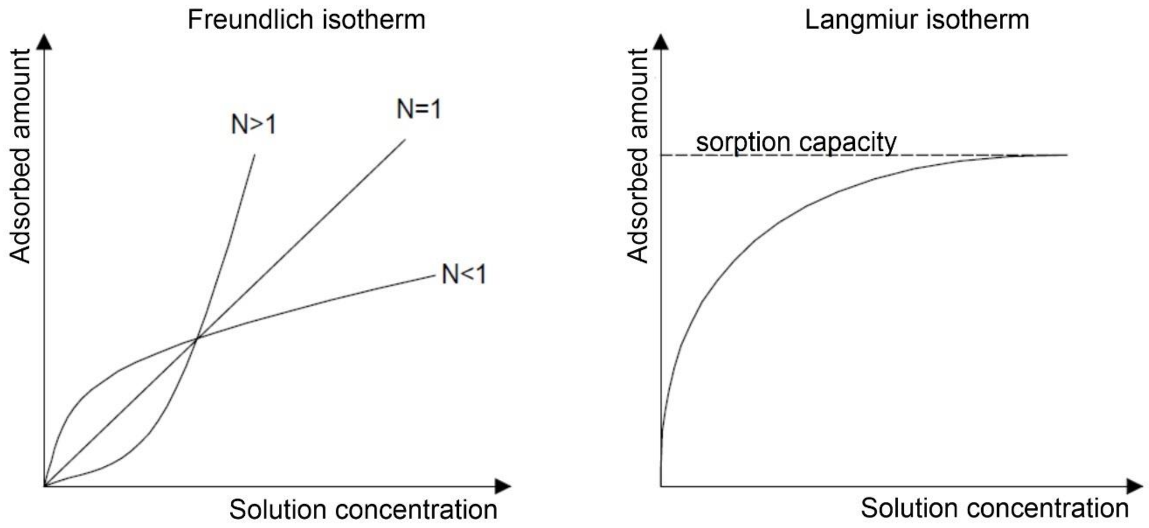


Figure 1. *The Freundlich and Langmiur isotherms (Kovács, 2004)*

In natural adsorption processes the Langmuir and the Freundlich adsorption processes are existed together, the ratio of these two processes will determine which isotherm will describe better the complete system (Czinkota, 1994).

In contradistinction to batch tests the breakthrough curve experiments are dynamic investigations where the dynamic of adsorption processes could be determined. In this test, solution with constant concentration is seeped through a column filled with the investigated soil. The flow rate of solution with C_0 initial concentration is also constant. In the column there is a mass transfer zone continuously moving in the direction of flow where adsorption process happen *(Figure 2)*. The shape of the concentration change in the mass transfer zone is a sigmoid curve, where the actual C shows the development of adsorption. When adsorption happened in a zone, the sites are filled with adsorbates the C value become equivalent to C_0, from this point only exchange of adsorbates happens in this zone. Investigation of process in time at the outflow point of column the point when the concentration of adsorbate appears is called C_b breakthrough point *(Figure 2)*. The concentration of adsorbate in the outflow solution is continuously increased to the point of C_d, where the concentration is equal to initial concentration. The interval between C_b and C_d is breakthrough zone *(Figure 2)*. From the equation fitted to the measured concentration change the main transport parameters can be derived.

The mathematical base of breakthrough curve is the 1D transport equation:

$$R\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} - \mu c + \gamma \tag{6}$$

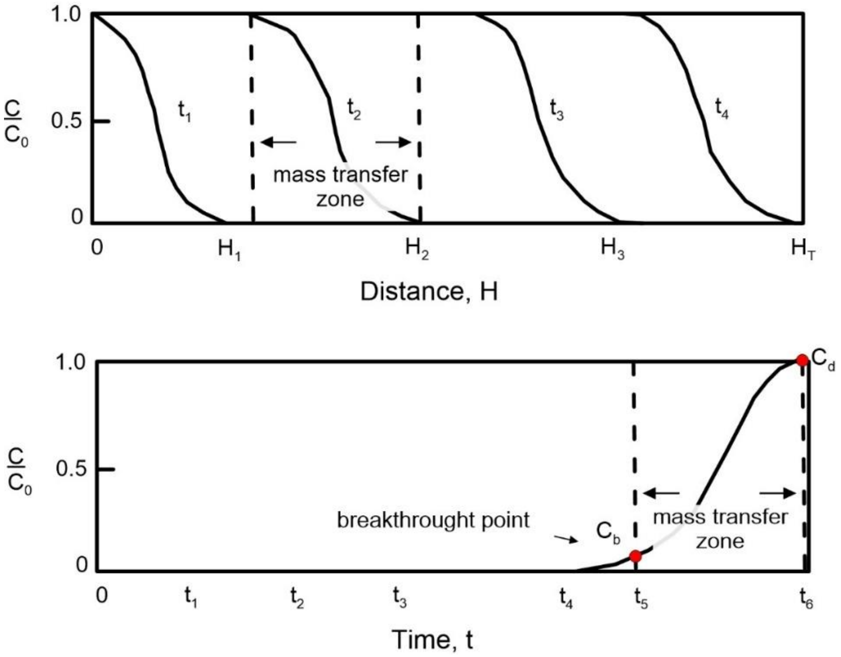


Figure 2. *The change of concentration profile in function of distance in the column and time during breakthrough process* (Geankopolis, 1993)

where, t is the time [s], c is the concentration [mg·L^{-1}] at distance x [m] from the column inlet, D is the hydrodynamic dispersion coefficient [m^2·s^{-1}], v is average R the dimensionless retardation factor reflects how strong the solute is retarded by adsorption.
With the following boundary conditions

$$c(x,0) = C_i$$

$$c(0,t) = \begin{cases} C_0 & 0 < t < t_0 \\ 0 & t < t_0 \end{cases}$$

$$\frac{\partial c}{\partial x}(\infty, t) = 0$$

where C_i is the initial concentration in the column, C_0 is the input concentration, t_0 is the duration of concentration impulse, the analytical solution of equation 6 (Bear, 1972) (Van Genuchten, 1981) (Van Genuchten & Alves, 1982) is

$$c(x,t) = \begin{cases} \frac{\gamma}{\mu} + \left(C_i - \frac{\gamma}{\mu}\right) A(x,t) + \left(C_0 - \frac{\gamma}{\mu}\right) B(x,t) & 0 < t < t_0 \\ \frac{\gamma}{\mu} + \left(C_i - \frac{\gamma}{\mu}\right) A(x,t) + \left(C_0 - \frac{\gamma}{\mu}\right) B(x,t) - C_0 B(x, t - t_0) & t < t_0 \end{cases} \tag{7}$$

where

$$A(x,t) = e^{\left(\frac{-\mu t}{R}\right)} \left\{1 - \frac{1}{2} erfc\left[\frac{Rx - vt}{2\sqrt{DRt}}\right] - \frac{1}{2} e^{\left(\frac{vx}{D}\right)} erfc\left[\frac{Rx + vt}{2\sqrt{DRt}}\right]\right\} \tag{8}$$

$$B(x,t) = \frac{1}{2} e^{\left[\frac{(v-u)x}{2D}\right]} erfc\left[\frac{Rx - ut}{2\sqrt{DRt}}\right] + \frac{1}{2} e^{\left[\frac{(v+u)x}{2D}\right]} erfc\left[\frac{Rx + ut}{2\sqrt{DRt}}\right] \tag{9}$$

and

$$u = v\sqrt{1 + \frac{4\mu D}{v^2}}$$

In our case 0 < t < t0

$$c(x,t) = \frac{\gamma}{\mu} + \left(C_i - \frac{\gamma}{\mu}\right) A(x,t) + \left(C_0 - \frac{\gamma}{\mu}\right) B(x,t) \tag{10}$$

where $\gamma = 0$ because there is no production and $C_i = 0$ because the concentration of adsorbate is 0 in the column before injection.

With this simplification the equation 10 is reduced to

$$c(x,t) = (C_0) B(x,t) \tag{11}$$

so the used form of breakthrough curve equation is

$$c(x,t) = \frac{C_0}{2}\left\{ e^{\left[\frac{\left(v - v\sqrt{1+\frac{4\mu D}{v^2}}\right)x}{2D}\right]} erfc\left[\frac{Rx - v\sqrt{1+\frac{4\mu D}{v^2}}t}{2\sqrt{DRt}}\right] + e^{\left[\frac{\left(v + v\sqrt{1+\frac{4\mu D}{v^2}}\right)x}{2D}\right]} erfc\left[\frac{Rx + v\sqrt{1+\frac{4\mu D}{v^2}}t}{2\sqrt{DRt}}\right]\right\} \tag{12}$$

where erfc is complementary of the Gaussian error function

$$erfc(x) = 1 - erf(x) = \frac{2}{\sqrt{\pi}}\int_x^{\infty} e^{-t^2} dt. \tag{13}$$

To presume the absorbate do not decay the equation 12 can simplify (Ogata & Banks, 1961).

$$C = C_0\left[\frac{1}{2} erfc\left(\frac{Rx - vt}{2\sqrt{DRt}}\right) + \frac{1}{2} e^{\frac{vx}{D}} erfc\left(\frac{Rx + vt}{2\sqrt{DRt}}\right)\right] \tag{14}$$

2. Materials and methods

Surface soil samples (SD and SV) were collected in the protected flood plain of Danube, near Solt on the WGS'84 coordinates of N46.49, E18.97 and N46.79, E19.03, respectively. To determine the collected soil samples characteristics labor investigations were performed (determination of liquid limit, plastic limit, and particle-size distribution analysis). The soil samples in the laboratory were dried to constant mass at 105 °C. Two laboratory test was performed: the batch test and breakthrough curve test.

In batch test stock solution of Zn and Mn were prepared in concentration of 25 ppm, 50 ppm, 100 ppm, 150 ppm and 200 ppm, respectively. After pretesting of adsorption capacity of the soil the reduction of used soil weight was necessary in the testing. The general soil : liquid ratio in batch tests is 1 : 10, in our case we modified to 1 : 100, so the weight of soil in the test was 0.10 g, the volume of added solution was 10 ml. After preparation of soil-liquid mixture, they were treated in continuously moving shaker for 24 hours. The separation of liquid phase was happened in centrifuge, after collection of liquid samples their element content was analyzed with an Agilent MP-AES instrument.

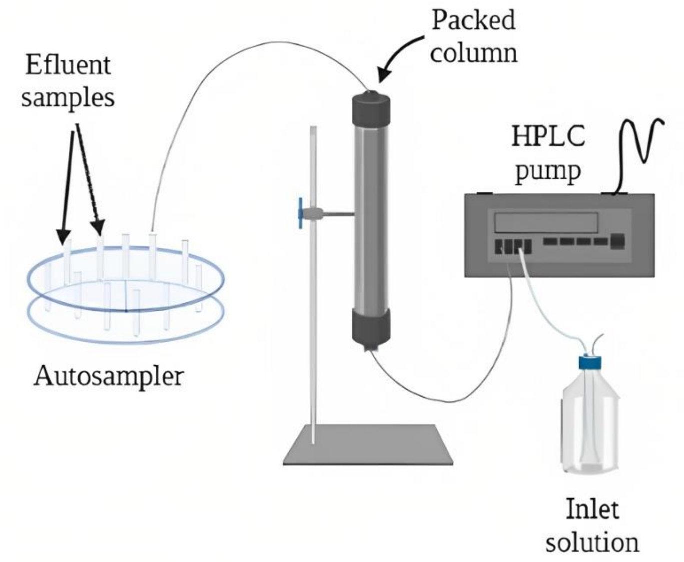


Figure 3. *The system of breakthrough curve experiment* (Borjini, 2021)

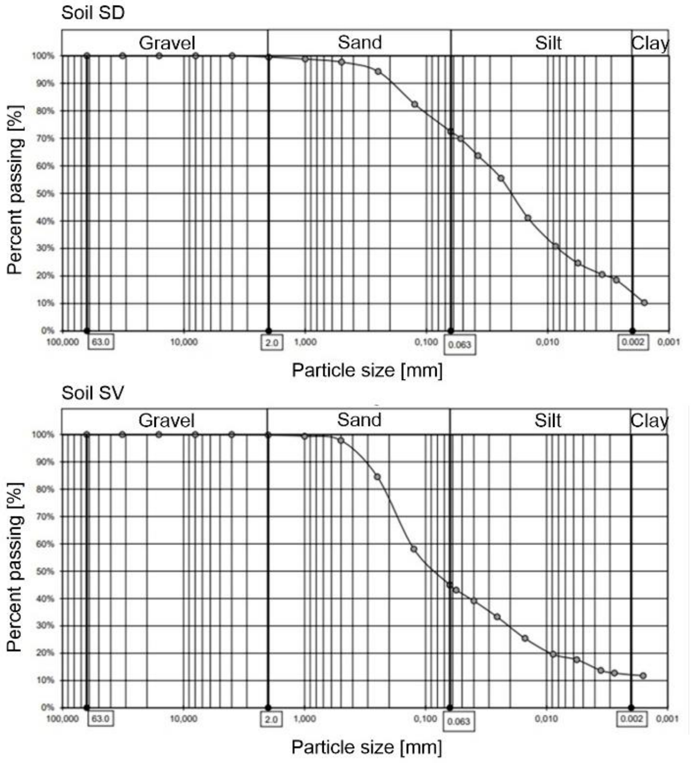
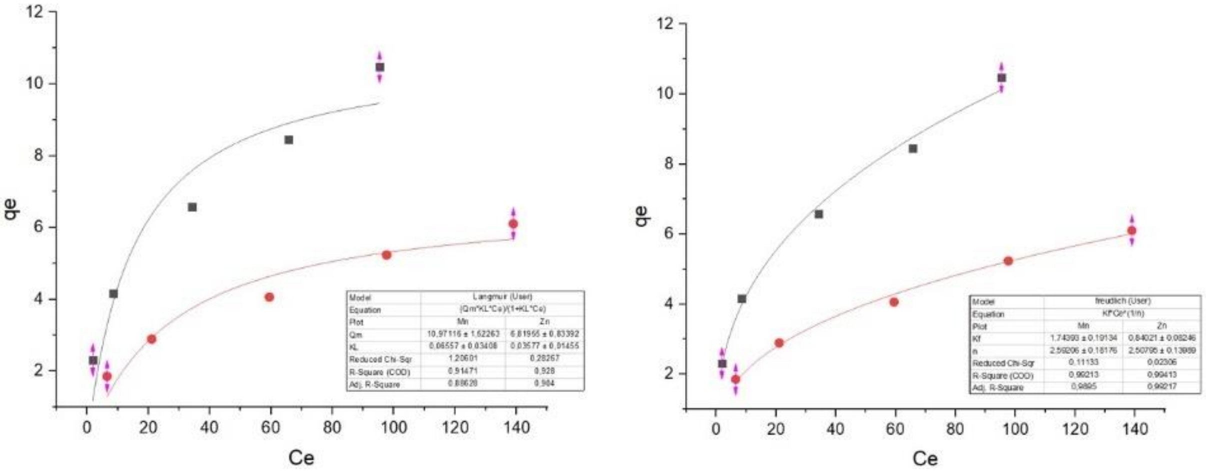


Figure 4. *Results of particle-size distribution analysis for soil SD and SV*

The system of breakthrough curve test is introduced on *Figure 3*. Stock solution of Zn and Mn were prepared in concentration 100 ppm. The packed column was filled with soil-sand mixture. Alone the soil had significant hydraulic resistivity, and too high adsorption capacity which would prevent the performance of test but dilution by sand could manage the problem. 190 g of inert, quartz sand was added to 10 g of soil then the soil-sand mixture was filled into the 25 cm long column, which had the diameter 0.9 cm. An HPLC pump keep the 1 [ml·min^{-1}] continuous flow rate of stock solution during test. The effluent solution was collected by an autosampler into 6 ml sample units and was analyzed with an Agilent MP-AES instrument.

3. Result

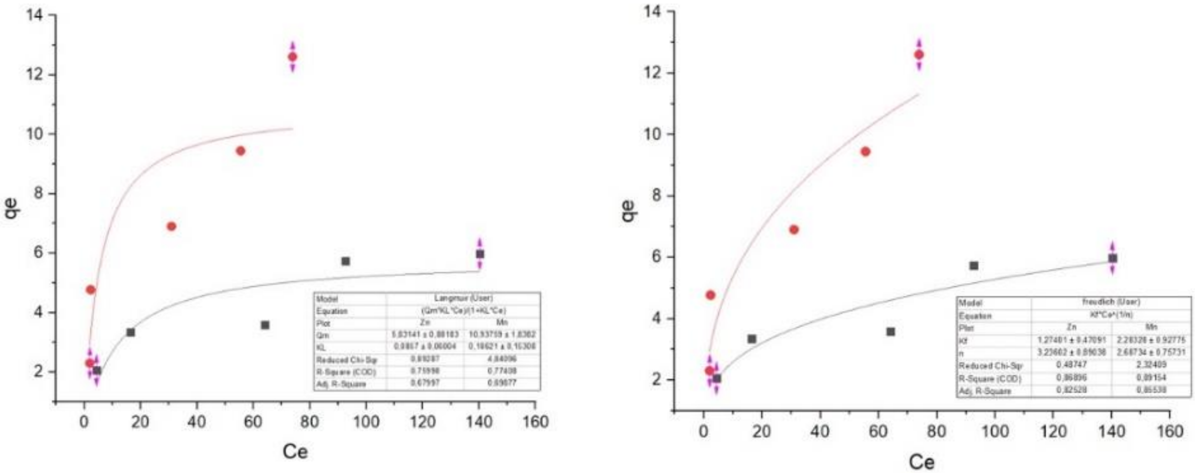
Soil SV



Model	Langmuir (User)	
Equation	(Qm*KL*Ce)/(1+KL*Ce)	
Plot	Mn	Zn
Qm	10,97116 ± 1,62263	6,81955 ± 0,83392
KL	0,06557 ± 0,03408	0,03577 ± 0,01455
Reduced Chi-Sqr	1,20601	0,28267
R-Square (COD)	0,91471	0,928
Adj. R-Square	0,88628	0,904

Model	freudlich (User)	
Equation	Kf*Ce^(1/n)	
Plot	Mn	Zn
Kf	1,74393 ± 0,19134	0,84021 ± 0,08246
n	2,59206 ± 0,18176	2,50795 ± 0,13989
Reduced Chi-Sqr	0,11133	0,02306
R-Square (COD)	0,99213	0,99413
Adj. R-Square	0,9895	0,99217

Soil SD



Model	Langmuir (User)	
Equation	(Qm*KL*Ce)/(1+KL*Ce)	
Plot	Zn	Mn
Qm	5,83141 ± 0,88183	10,93759 ± 1,8382
KL	0,0867 ± 0,06004	0,18621 ± 0,15308
Reduced Chi-Sqr	0,89287	4,84096
R-Square (COD)	0,75998	0,77408
Adj. R-Square	0,67997	0,69877

Model	freudlich (User)	
Equation	Kf*Ce^(1/n)	
Plot	Zn	Mn
Kf	1,27401 ± 0,47091	2,28328 ± 0,92775
n	3,23602 ± 0,89038	2,68734 ± 0,75731
Reduced Chi-Sqr	0,48747	2,32409
R-Square (COD)	0,86896	0,89154
Adj. R-Square	0,82528	0,85538

Figure 5. *Results batch test for soil SD and SV*

According to the result of consistency investigations the soil samples are sandy clayey silt (SD $I_p = 9.1$) and sandy silty clay (SV $I_p = 15.64$). On the particle-size distribution curves *(Figure 4)*, in case of soil SD the ratio of silt fraction is 57%, while the ratio of clay fraction is 15%, respectively. In case of soil SV the ratio of silt fraction is 33%, while the ratio of clay fraction is 12%. These differences in presence of silt fraction can suggest that SD will have a higher adsorption capacity.

Table 1

The values of calculated Freundlich constants

K_F	*SV*	*SD*
Mn	**1.74**	**2.28**
Std. dev.	0.19	0.92
Zn	**0.84**	**1.27**
Std. dev	0.08	0.47

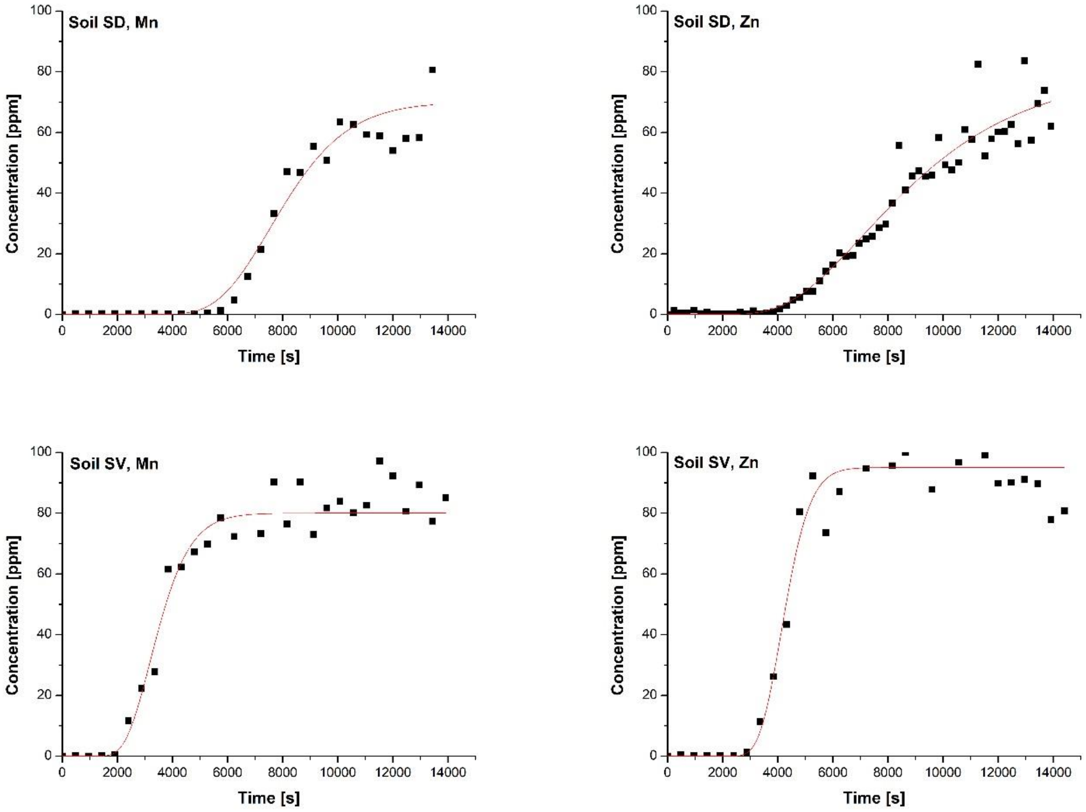


Figure 6. *Results breakthrough curve test for soil SD and SV*

To evaluate the result of batch test, a program (OriginLab Origin 6.0) was used to fit the non-linear equation of Langmuir and Freundlich isotherms *(Figure 5)*. The fitting of isotherms is better in case of Freundlich equation (SV $R_{Mn}^2 = 0.99$, $R_{Zn}^2 = 0.99$, SD $R_{Mn}^2 = 0.87$, $R_{Zn}^2 = 0.89$), so the ion exchange characterizes the adsorption process not the saturation of adsorption places. The value of Freundlich constant is higher for soil SD ($K_{f,Mn} = 2.28$, $K_{f,Zn} = 1.27$) than for soil SV ($K_{f,Mn} = 1.74$ $K_{f,Zn} = 0.84$) in case of both heavy metal *(Table 1)*, so our first suggestion related to higher adsorption capacity of SD according to silt fraction difference was proved in this investigation. From the investigation the higher adsorption of Mn is also proved, because in case of every setup of test the received K_f constant is higher for this metal.

During the breakthrough curve test directly the adsorption constant cannot be determined because the breakthrough equation just contain retardation factor (R). But according to the following equation (10) the adsorption constant, the distribution coefficient can be calculated.

$$R = 1 + \frac{\rho}{n_0} \cdot K_d \tag{10}$$

where ρ is the bulk density, n_0 is the effective porosity and K_d is distribution coefficient. The results of breakthrough curve experiments show the same adsorption differences of soils like batch test *(Figure 6)*. Because during built-in of bed in the column the porosity can change from this aspect the calculation of distribution coefficient is preferred to make the adsorption processes comparable *(Table 2)*. The soil SD has higher adsorption capacity than soil SV. To compare the different metals the Mn ($K_d = 2.99$) has higher adsorption than Zn ($K_d = 2.37$).

Table 2

The calculated K_d values from R retardation factor

Soil	Metal	R	K_d
SV	Zn	7.58	1.86
SV	Mn	6.32	1.55
SD	Zn	9.77	2.37
SD	Mn	12.36	2.99

4. Summary

According to the silt ration difference of soil SD and soil SV the adsorption capacity difference of soils was proved. In static adsorption batch test the adsorption performance of soil SD was better compared to soil SV, and from the aspect of metals the adsorption of Mn was more intensive compared to Zn. The adsorbed amount of metals in batch test can be understood as a maximum that can adsorb in the investigated soil because there is enough residence time to reach the equilibrium. In case of breakthrough curve experiment, the adsorption will just characterize that flow condition in which the experiment happen. The change in flow rate will determine the residence time, so there will be new equilibrium in adsorption. This is the reason why it is important to correctly determine the hydraulic regime during modeling of transport of heavy metals because the adsorption of heavy metals will differ in case of different flow velocities. In case of a heavy metal contamination the soil SD will adsorb the metals better than soil SV, so their spread will be significantly slower.

5. Acknowledgements

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