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APPLICATION OF COLUMN TESTS TO DERIVE TRANSPORT PARAMETERS OF MANGANESE IN MINE WASTE DUMP MATERIAL OF RUDABÁNYA

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Abstract: The most accurate method to create a transport model of an area is to determine the transport parameters of a contaminant in the investigated porous media. The batch and column tests are the tools that can be used to derive this information. To describe the transport process in a column, 1D transport equation is applicable therefore the equation's analytical solution becomes possible. In our work, two-column test setups were investigated from the aspect of their accuracy in the determination of longitudinal dispersivity, retardation factor, and irreversible reaction rate constant, respectively. In the first measurement method, a solution with constant concentration (0.01 M Mn solution) was percolated through the column filled with mine waste dump material. In the second measurement method, distilled water was percolated through the column continuously but in a moment an impulse amount of manganese (10 ml 0.5 M Mn solution) was injected into the column at its bottom. The first measurement served the breakthrough curve (BTC), and the second measurement resulted the impulse curve (IMP). The retardation factor of Mn found in the media is similar in both measurement setups (R_{BTC}=1.87, R_{IMP}=1.47). The value of the irreversible reaction rate constant differs in the two experiments; an order of magnitude difference was found between the result of the breakthrough test ($\mu_{BTC}=6.94\cdot10^{-5}$ 1/s) and the impulse test ($\mu_{IMP}=2.09\cdot10^{-4}$ 1/s).

Keywords: *heavy metal, breakthrough test, mine waste dump, irreversible reaction rate*

1. INTRODUCTION

Heavy metal contaminations related to various human activities are crucial environmental hazards waiting for management and solutions (Sharma and Reddy, 2004). With their high pervasion, persistence, and toxicity they threaten ecosystem services, and they potentially have human health implications (Moulatlet et al., 2023). Potentially toxic heavy metals like Cd, Cr, Cu, Hg, Mn, Ni, Pb and Zn could be released during the mining-, industrial-, agricultural-, traffic- and waste-deposing activity (Heltai et al., 2018).

PRE-PROOF

During the mining and milling processes, four types of waste could be generated which could have significant environmental hazards of their heavy metal content, like mine waste, tailings, dump heap leach, and acid mine water (Anju and Banerjee, 2010). The exploited ore never can separate from secondary rocks, so the mine waste always has significant heavy metal content (Zou and Ren, 2023) but their mobility is significantly dependent on their mineralogical forms. Generally, in the mines, heavy metals can be found in sulfide-bearing ores, and between them iron sulfide is an outstanding one that can be oxidized quickly after they are brought to the surface. The oxidation of iron (and after its hydrolysis) releases a significant amount of acid into the environment (Stumm and Morgan, 1996). This process is Acid Mine Drainage (AMD) which is another well-known environmental hazard related to mines (Zheng et al., 2023) occurring not just in mine waste dumps but also in the open pits and drifts. Water affected by AMD has a very low pH ($pH \approx 2$-3) and it has a high reduction-oxidation potential which serves the proper conditions for heavy metals to be dissolved and transported with the percolating water. Then contaminated water can flow on the surface as surface runoff threatens surface water resources or after infiltration through the vadose zone, it can deteriorate aquifers (Tomiyama and Igarashi, 2022).

Implementation of remediation is not always necessary when heavy metal contamination occurs but to constrain and forecast the movement of the plume is crucial. To manage heavy metal contaminations in groundwaters the transport models are frequently used tools (Kresic, 2007). In porous media of mine waste dumps, the dissolved heavy metals are affected by the following transport processes: advection, hydrodynamic dispersion, chemical–biochemical reactions such as adsorption-desorption reactions, acid-base reactions, solution-precipitation reactions, oxidation-reduction reactions, ion pairing or complexation, and microbial cell synthesis (Freeze and Cherry, 1979). An appropriate transport model describing the investigated environmental situation postulates reliable parameters. These parameters could be determined in column experiments which are commonly used procedures (Kang et al., 2021, Mufalo et al., 2023). Transport of heavy metals in columns is a special case of transport modeling that can be described by 1D transport equations therefore application of an analytical solution is possible. In transport equations, the concentration change in function of time or location is determined by a couple of parameters but not all of them can be measured easily as flow velocity, initial concentration, or porosity. The determination of the dispersion constant, retardation factor, and irreversible reaction rate constant is an iterative work by the fitting of the properly selected form of the 1D transport equation which depends on boundary conditions. The retardation factor, the dispersion constant can be determined according to Ogata and Banks's solution (1961) that presumes reversible processes as reversible adsorption (Czinkota et al., 2006). But in more complex situations additional parameters such as first-order irreversible reaction rate constant and first-order production should be involved (Van Genuchten, 1981) to solve the transport problem.

PRE-PROOF

1.1. Study area

Rudabánya is an old, abandoned mine site in north-east Hungary located in the Aggtelek-Rudabánya Mountains (Fig. 1a). Geological formations of the area are building units of the Silicic Superunit of the ALCAPA region. The elements of the Silicic Superunit are Upper Permian- Lower Triassic evaporites, Lower Triassic siliciclastic formations and carbonates, and Middle-Upper Triassic and Jurassic carbonates (Szentpétery and Less, 1986). The origin of mineralization occurs in several superposed periods (Földessy et al., 2010). The first period of ore formation was a synsedimentary, stratiform, sedimentary-exhalative Pb-Zn accumulation associated with barite and pyrite (Nemeth et al., 2013). After, probably in the Cretaceous age, during the process of metasomatism siderite was generated in the Lower-Middle Triassic carbonates (Bodor et al., 2016). In the last phase of ore formation pyrite-bearing massive sulfide-filled veins with later lead-, zinc-, silver-, and copper enrichments were generated (Földessy et al., 2010).

The open pit and underground iron ore (siderite and limonite) mining activity took place in Rudabánya between 1872 and 1985 resulting in a lot of mine waste dumps with significant heavy metal content (nowadays these waste dumps are under investigation as secondary raw material (Földessy et al., 2010). In the closure procedure of the mine, mechanical recultivation was performed by the explosion of steep walls

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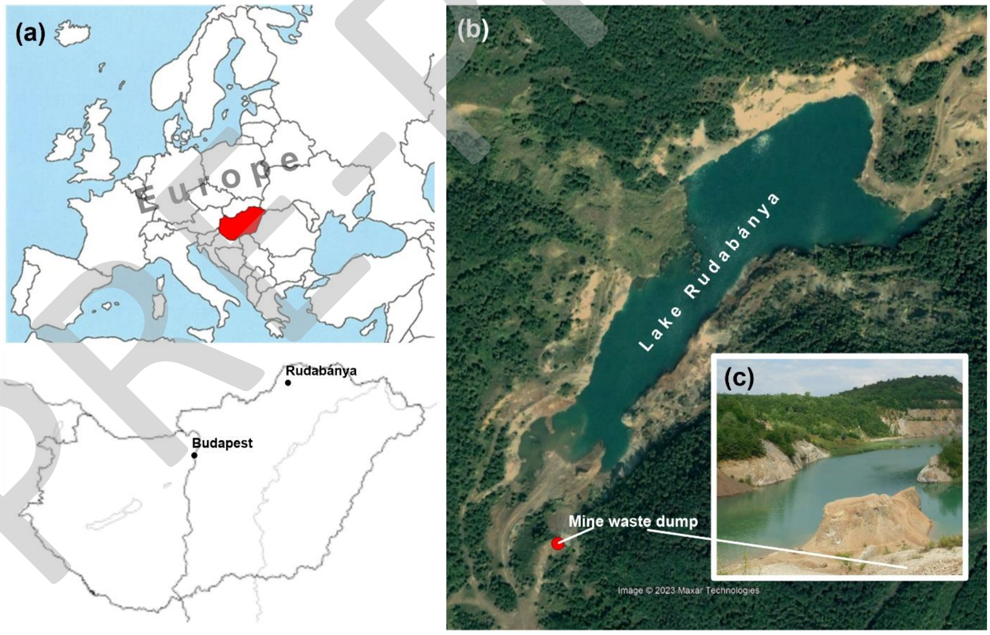

Figure 1

(a) Location of abandoned mine site of Rudabánya, (b) Location of the investigated mine waste dump, (c) View of the lake from the sampled mine waste dump

of the open pit and by filling up of emptied areas but the open pit was not filled up where a lake was formed from the concentration of surface and subsurface waters (Balla et al., 1987). Mine waste dumps all over the mine site were not recultivated, their environmental impact now is under investigation in our research.

2. MATERIALS AND METHODS

2.1. Soil sampling

Mine waste dump material (MWDM) was collected from the upper 20 cm depth of a waste dump on the abandoned mine site of Rudabánya (Fig. 1b-c). Because the research work aimed to answer the vulnerability of surface waters against heavy metal leaching from waste dumps, the samples were collected from waste dumps near Lake Rudabánya. The collected material was placed in a PE bag and immediately brought to the laboratory. The drying of the sample happened at 105°C until reaching mass constancy, then bigger aggregates were crushed in a mortar to prepare for sieving. Particles above a diameter of 8 mm were removed from the sample because they were not fitted to the inner dimensions of the column, and their lack did not influence the result of the column test because the reactive particles can be found below a diameter of 0.2 mm (Plassard et al., 2000). Based on the grain size distribution of the filling material, the prepared sample for the column test consisted of approximately 70% gravel, 21.5% sand, 7.5% silt, and 1% clay.

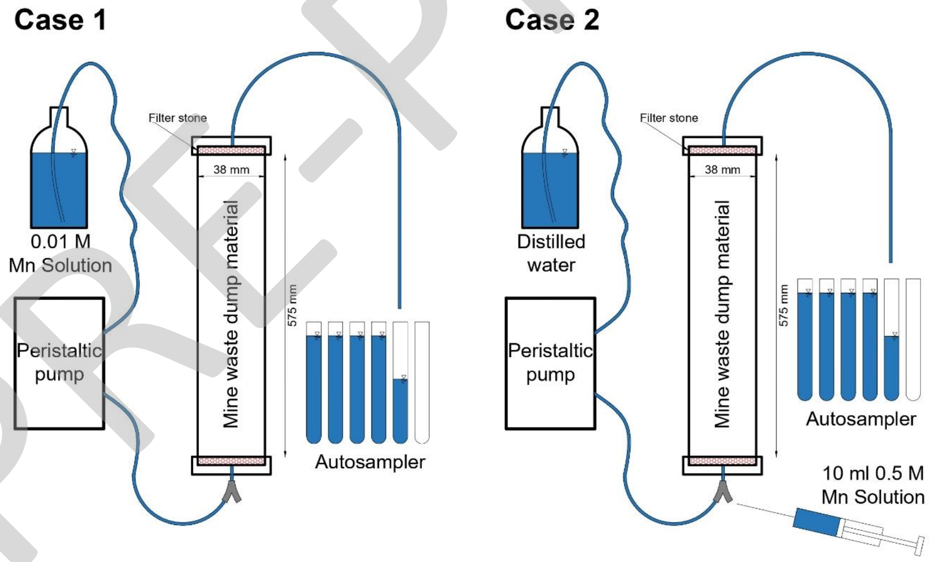

Figure 2
Schematic view of the experimental setup

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2.2. Column experiment

Prepared MWDM was packed into a 575-mm length and 38-mm inner diameter Plexiglas column, yielding an approximate packing density of 1.96 g/cm^3 and a porosity of 0.4 v/v determined according to average particle density from pycnometer measurements (Tan, 1995). The column was flushed with 10 pore volumes of distilled water to remove contaminants and to check the hydraulic stability of built-in materials. Metal solutions were then fed into the column from the bottom with a flow rate of ca. 24 ml/min which meant 0.04 cm/s flow velocity. Two-type of break through experiments were performed; in the first case an Mn solution (pH=6 at 25°C) with a constant concentration of 0.01 M was driven through the column, in the second case 10 ml of 0.5 M concentration of Mn solution (pH=6 at 25°C) was injected into the column at its bottom, then only just distilled water was fed into the column (Fig. 2). The effluent fluid in both cases was collected in 10 ml units until the total flow-through volume exceeded 5 times the pore volume. The collected samples were analyzed by a UniCam 929 AAS. In the following, we refer to the first measurement setup as a breakthrough test (BTC) (described later by Equation 6). and to the second measurement as an impulse test (IMP) (described later by Equation 9).

2.3. Mathematical background of experiments

The governing equation describes the transport of any compound in porous media in case of constant volumetric moisture content and volumetric fluid velocity (Van Genuchten, 1981)

$$R\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} - \mu c + \gamma \tag{1}$$

where R is the retardation factor, c is the solution concentration (mg/L), t is time (s), D is dispersion coefficient (cm^2/s), x is the distance (cm), v is pore-water velocity (cm/s), μ is irreversible reaction rate constant (decay) and γ is production coefficient (Goode and Konikow, 1989).

We apply the following boundary conditions (Van Genuchten, 1981)

$$c(x,0) = C_i$$
$$c(0,t) = \begin{cases} C_0 & 0 < t < t_0 \\ 0 & t > t_0 \end{cases}$$
$$\frac{\partial c}{\partial x}(\infty, t) = 0$$

where C_i is initial concentration, the C_0 is input concentration and t_0 is duration of solute pulse. The analytical solution of Equation 1 is

PRE-PROOF

$$c(x,t) = \begin{cases} \text{and}\, \frac{\gamma}{\mu} + \left(C_i - \frac{\gamma}{\mu}\right) A(x,t) + \left(C_0 - \frac{\gamma}{\mu}\right) B(x,t) & 0 < t < t_0 \\ \text{and}\, \frac{\gamma}{\mu} + \left(C_i - \frac{\gamma}{\mu}\right) A(x,t) + \left(C_0 - \frac{\gamma}{\mu}\right) B(x,t) - C_0 B(x, t - t_0) & t > t_0 \end{cases} \tag{2}$$

where

$$A(x,t) = e^{\left(\frac{-\mu t}{R}\right)} \left\{ 1 - \frac{1}{2} erfc\left[\frac{Rx - vt}{2\sqrt{DRt}}\right] - \frac{1}{2} e^{\left(\frac{vx}{D}\right)} erfc\left[\frac{Rx + vt}{2\sqrt{DRt}}\right] \right\} \tag{3}$$

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

and

$$u = v\sqrt{1 + \frac{4\mu D}{v^2}} \tag{5}$$

In out experimental setup, in the interval of

$0 < t < t_0$

there was no production ($\gamma = 0$), and there was no initial concentration of Mn in the column (C_i=0), too. With these boundary conditions, the following equation describes 1D transport (BTC)

$$BTC = c(x,t) = \frac{C_0}{2} \left\{ e^{\left[\frac{\left(v - v\sqrt{1 + \frac{4\mu D}{v^2}}\right)x}{2D}\right]} erfc\left[\frac{Rx - v\sqrt{1 + \frac{4\mu D}{v^2}}t}{2\sqrt{DRt}}\right] + e^{\left[\frac{\left(v + v\sqrt{1 + \frac{4\mu D}{v^2}}\right)x}{2D}\right]} erfc\left[\frac{Rx + v\sqrt{1 + \frac{4\mu D}{v^2}}t}{2\sqrt{DRt}}\right] \right\} \tag{6}$$

where erfc is the complementary function of Gauss error function

$$erfc(x) = 1 - erf(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-t^2} dt \tag{7}$$

PRE-PROOF

By the elimination of irreversible reaction rate constant, the Equation 6 simplifies to

$$C = C_0\left[\frac{1}{2}erfc\left(\frac{Rx-vt}{2\sqrt{DRt}}\right)+\frac{1}{2}e^{\frac{vx}{D}}erfc\left(\frac{Rx+vt}{2\sqrt{DRt}}\right)\right] \tag{8}$$

as given by Ogata and Banks (1961).

We solve Equation 1 for instantaneous injection of pollutant mass ΔM, at the point x=0 and in time t=0. This type of initial condition can be expressed by means of Dirac-function (Kinzelbach, 1986, Kovács, 2004)

$$C_\delta(x,0) = \frac{M}{n_0AR}\delta(x) \tag{9}$$

where A is cross-sectional area of flow medium and Dirac-function δ(x) is defined as

$\delta(x) = 0$, when $x \neq 0$,

and

$\int_{-\infty}^{+\infty}\delta(x)dx = 1$, when $x = 0$.

When $C(\pm\infty, t) = 0$, the solution of Eq. 9 is

$$IMP = C(x,t) = \frac{M}{2An_0R\sqrt{\frac{\pi\alpha_L vt}{R}}}e^{\left(-\frac{\left(x-\frac{vt}{R}\right)^2}{\frac{4\alpha_L vt}{R}}\right)}e^{(-\mu t)} \tag{10}$$

where n_0 is effective porosity and α_L is longitudinal dispersivity.

To derive transport parameters fitting analysis of OriginPro 8.6.0 of OriginLab Co was used. In the following, Eq. 6, Eq. 8 and Eq. 10 are used to determine the transport parameters of MWDM.

3. RESULTS

Three parameters were derived from experiments: retardation factor, longitudinal dispersivity (by neglecting the molecular diffusion, it can be calculated from hydrodynamic dispersion), and irreversible reaction rate constant (Figs. 3-4).

Longitudinal dispersivity is not generally usable information because this parameter only just characterizes the investigated scale of the model. This parameter will be higher in the mine waste dumps because the ratio of the spatial extension of the

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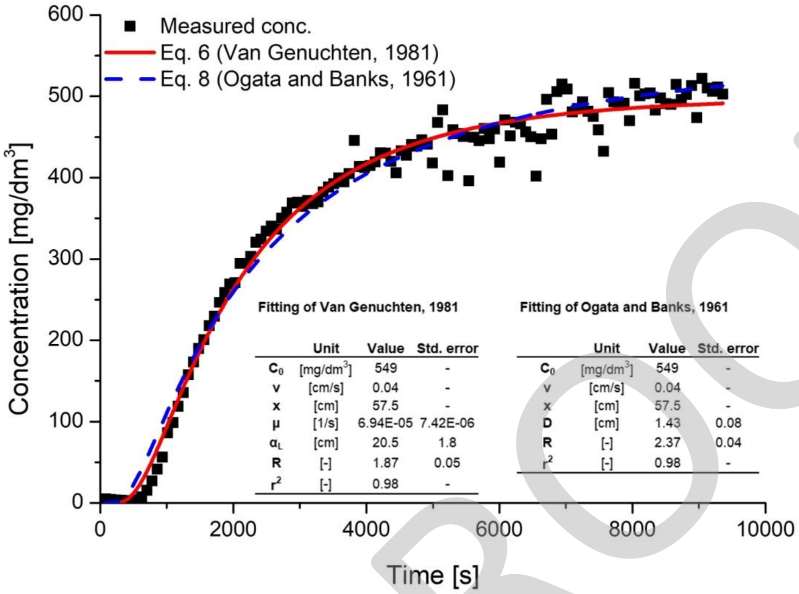


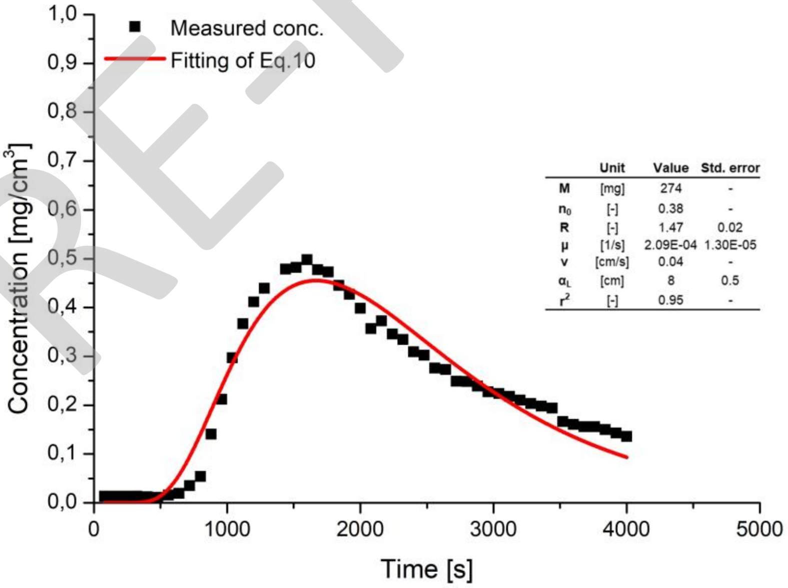
Fitting of Van Genuchten, 1981

	Unit	Value	Std. error
C_0	[mg/dm^3]	549	-
v	[cm/s]	0.04	-
x	[cm]	57.5	-
μ	[1/s]	6.94E-05	7.42E-06
α_L	[cm]	20.5	1.8
R	[-]	1.87	0.05
r^2	[-]	0.98	-

Fitting of Ogata and Banks, 1961

	Unit	Value	Std. error
C_0	[mg/dm^3]	549	-
v	[cm/s]	0.04	-
x	[cm]	57.5	-
D	[cm]	1.43	0.08
R	[-]	2.37	0.04
r^2	[-]	0.98	-

Figure 3
Results of Mn solution breakthrough test



	Unit	Value	Std. error
M	[mg]	274	-
n_0	[-]	0.38	-
R	[-]	1.47	0.02
μ	[1/s]	2.09E-04	1.30E-05
v	[cm/s]	0.04	-
α_L	[cm]	8	0.5
r^2	[-]	0.95	-

Figure 4
Result of Mn impulse test

PRE-PROOF

model and longitudinal dispersivity changes between 10:1 and 100:1 (Kinzelbach, 1986), but it could be higher than 100:1 in larger scales (Kovács and Szanyi, 2005). The values of longitudinal dispersivity in the breakthrough test and impulse test are 20.5 cm and 8 cm, respectively.

The retardation factor describes the adsorption of the component in the system. The retardation factor of Mn in the MWDM is similar in both measurement setups (R_{BTC}=1.87 (Fig. 3, Van Genuchten solution) and R_{BTC}=2.37 (Fig. 3, Ogata and Banks solution), R_{IMP}=1.47 (Fig. 4)). The difference experienced between the resultant parameters of Van Genuchten solution and Ogata and Banks solution of breakthrough test comes from the neglection of irreversible reaction rate in Equation 8 (Ogata and Banks solution). This difference highlights how important to enumerate the possible processes during heavy metal transport.

The value of the irreversible reaction rate constant differs in the two experiments; there is an order of magnitude difference between the result of the breakthrough test ($\mu_{BTC}=6.94 \cdot 10^{-5}$ 1/s, (Fig. 3, Van Genuchten solution) and the impulse test ($\mu_{IMP}=2.09 \cdot 10^{-4}$ 1/s (Fig. 4)). Because the determination of transport parameters is based on the same fitting analysis, the difference in irreversible reaction rate constant is probably related to the different sensitivity of transport equations (Eq. 6 and Eq. 10) for this parameter.

4. DISCUSSION

In case of high retardation factor the breakthrough of the heavy metal is slower in the investigated material. According to the definition of retardation factor values greater than unity indicate sorption (Amacher et al., 1986). Fonseca et al. (2011) found retardation factors for Zn R_{Zn}=6 and for Cu R_{Cu}=49 in loamy sand soil during mono-metal transport conditions. To compare the Mn retardation factor in our experiment the low values indicate low affinity of the component to adsorb, thus Mn can be considered a mobile element in the MWDM.

Although the adsorption of Mn is not determinant in the transport process its irreversible reaction rate constant significantly modifies the heavy metal concentration in the effluent fluid. In a column test aiming determination of the transport parameters of a solute, it is better to investigate first the possibility of irreversible material loss because it can cause significant differences between the determined parameters of the impulse test and breakthrough test. According to our investigation, it seems the impulse test is more sensitive on change of irreversible reaction rate constant compared to the breakthrough test but to prove this assumption further sensitivity analysis is needed.

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