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Proceeding Paper

Simulation of 1-d Solute Transport with Equilibrium-controlled Non-linear Sorption using MT3DMS †

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Abstract: Groundwater contamination is a rising worldwide issue, and it must be treated well as most of the world relies on it. Groundwater pollution occurs when undesirable substances in groundwater rise. Understanding, simulating, and predicting solute mobility in groundwater helps treat polluted groundwater. MT3DMS has been used to model contaminant movement with a non-linear Freundlich sorption isotherm. MT3DMS stands for "Modular three-dimensional multispecies transport model". MT3DMS software has several categories of solute transport solution techniques like FDM and the higher-order finite-volume TVD method in a unique single code. Applying the combination of these solution techniques is believed to give the best possible solution with greater precision and accuracy. In the current work, the benchmark problem (P2) of the MT3DMS package was taken, and the chemical reaction package was modified according to our problem. Multiple simulations were run with different adsorption capacities and intensities, incorporating the nonlinear Freundlich sorption isotherm. After that analysis of BTC trends, at a position 8 cm from the source, the pulse input of contamination was discharged for 160 seconds. The simulation lasted 1500 seconds. The observation output files were imported to plot BTCs for trend analysis and visualize simulation results. After comparing the various BTCs, it was found that the adsorption capability of porous medium enhances retention capacity, so contaminants are sorbed and retarded by the solid phase more, slowing the contaminant movement and delaying the BTC peak. For similar adsorption capacity at lower adsorption intensity, the solid retains more contaminant and the peak is attenuated as well as delayed, but as the adsorption intensity increases, the relative concentration in the aqueous phase increases, and the peak is enhanced early as the solid retains less contaminant.

Keywords: Groundwater contamination; Sorption; MT3DMS; Simulation; Breakthrough curves (BTC)

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1. Introduction

Groundwater pollution is one of the major emerging challenges globally [1]. Since groundwater is a potential source of water for use in daily life and for basic usages like drinking, it should be strongly considered for assessment and the design of remedial techniques for its pollution [2]. Generally, it is assumed that the migration of a reactive solute in any porous media with groundwater is assumed to be driven by a linear sorption isotherm [3]. Though research efforts are focused on determining the non-linear isotherms' functional structure, principles, and features, often hydrologists and environmental engineers are also engrossed in predicting the plume propagation and breakthrough curves for multiple or a single set of contamination schemes and scenarios. For the present study, we will take the pulse concentration source with a single contaminant for a better understanding of its fate and transport with nonlinear sorption. The processes responsible for the transport of solutes in groundwater as per [4] are advection, mechanical Dispersion, molecular diffusion, sorption and colloid transport. [5] They used HYDRUS 1D/2D software for the simulation of solute transport, making variations in critical parameters of flow and transport for various soil conditions. [6] The study was conducted for the remediation of metal contaminants in groundwater and greywater. Heavy metals were extracted efficiently from test samples using the adsorption process.

2. Methodology

2.1. MT3DMS

For this study, the simulation was done with the help of MT3DMS software downloaded from the website of the U.S. Geological survey department (https://www.usgs.gov). MT3DMS can be used to simulate various physical and chemical changes undergoing solute transport processes. Also, there is independence in the selection of different boundary conditions. The basic chemical reaction package named RCT can solve single species with conditions like equilibrium-controlled or non-linear sorption and 1st order kinetic reactions.

Governing equation of solute transport model in MT3DMS is:

$$R\theta\frac{\partial\bar{c}}{\partial c}=\frac{\partial}{\partial x_i}\left\{\theta Dij\frac{\partial c}{\partial x_j}\right\}-\frac{\partial}{\partial x_i}(\theta v_i C)+q_s Cs-q_s' C-\lambda_1\theta C-\lambda_2\rho_b\bar{C} \quad (1)$$

(θ = Porosity of media, dimensionless; C = Dissolved concentration in aqueous phase; ML^{-3} , t = time; Seconds, V_i = seepage velocity; LT^{-1}, q_s = discharge per unit volume of medium; T^{-1}, q'_s =rate of change in GW storage; T^{-1}, ρ_b=bulk density medium; ML^{-1}, $\bar{C}$= sorbed contaminant concentration on the medium; MM^{-1}, λ_1 = 1st order reaction rate for dissolved phase; T^{-1}, λ_2 =1st order reaction rate for the sorbed phase, T^{-1} ; R = Retardation factor)

2.2. Chemical reaction package

For the simulation in MT3DMS, the assumption of equilibrium condition is made generally, that sorption is instantaneous and the sorption reaction is faster as compared to seepage velocity.

As we know, at constant temperature, the sorption process is explained by the functional relationship between sorbed and dissolved concentrations. It is termed the sorption isotherm. The retardation factor (R), described in governing equation (1), is commonly used to integrate equilibrium-controlled sorption isotherms into the transport model. Since, this study incorporates the non-linear Freundlich sorption isotherm, The empirical equation for the same is:

$$\bar{c}=K_f c^a \quad (2)$$

(K_f = Freundlich constant (Adsorption capacity/partition factor), (L^3M^{-1}); a = Freundlich exponent (adsorption intensity) dimensionless.).

Retardation factor can be defined as:

$$R=1+\frac{\rho_b}{\theta}\frac{\partial\bar{c}}{\partial c}=1+\frac{\rho_b}{\theta}aK_f C^{a-1} \quad (3)$$

2.3. Transport model Formation and Validation

For this study, the same problem is opted as demonstrated in [7], considering Freundlich isotherms, and the input files for the same problem are given in benchmark problem P2 of the MT3DMS software. For the creation of input files according to our study, desired changes in existing input files of the chemical reaction package of MT3DMS input files (RCT package) were made, and modifications were made as per directions suggested in the MT3DMS user manual [8] for the creation of desired input files.

Model parameters were taken as follows: Grid-space(ΔX) = 0.160 cm, Dispersivity(α_L) = 1.0 cm, GW seepage-velocity(v)= 0.1 cm/s, Porosity(θ) = 0.37, Bulk density(ϱb) =1.587 g/cm3, Source concentration (Co) = 0.05 mg/l, Pulse Input time (t_o)= 160 seconds.

Here, due to the low Peclet number (0.16), the transport mechanism will not be advection-dominating and the migration of the solute will be due to sorption.

Initial and boundary conditions for our model are provided as follows:

$$C\ (x, 0) = 0 \tag{4}$$

$$-\theta D\left(\frac{\partial C}{\partial x}\right) + qC\,\Big|(x = 0) = \begin{cases} fo & 0 < t < to \\ 0 & t > to \end{cases} \tag{5}$$

$$\frac{\partial C}{\partial x}(\infty, t) = 0 \qquad\qquad t > 0 \tag{6}$$

The boundary conditions for the flow model in this study involve setting constant hydraulic head values at both ends of the model domain. This is done by assigning an arbitrary hydraulic head value to achieve the desired Darcy flux. As the flow field is steady-state, only one stress period is necessary for the flow model. However, the transport model requires two stress periods to account for changes in source concentration.

In the transport model used in this study, the boundary conditions involve a specified total mass flux (third-type) on the left side and zero dispersive mass flux (second-type) on the right side. To approximate the third-type boundary condition, the advective mass flux is specified using the rate of inflow or outflow across the boundary (represented by q). To implement this in the test problem, the concentration of the inflow at the constant-head node on the left is set to 0.05 mg/L for the first and second stress periods, respectively. The second-type boundary condition is addressed by placing it far enough from the source to prevent the plume from reaching it within the given simulation time.

The validation of the model was done with the benchmark problem, and the result obtained from the analytical method were like the numerical simulation.

2.4. Input files, Data and Simulation

Multiple simulations were run for this problem by altering the values within the range discussed below, and the output of each simulation was saved individually to avoid any possible error. The Chemical reaction input files package (RCT package) incorporating the nonlinear Freundlich sorption isotherm has two sorption parameters, SP_1=K_f and SP_2= a, and the input data variation was made with different sets of these two parameters as follows:

Set number-1 K_f =0.20 to 1.40 & a=0.70,
Set number-2 K_f =0.20 to 1.40 & a=0.60,
Set number-3 K_f =0.20 to 1.40 & a=0.80.

For the variation for 'K_f' (SP_1) and 'a' (SP_2) for above sets, the range for variation has been taken from [9], [10], [11] and [12]. All other input parameters and boundary conditions of the model remain unchanged and are applied as per the standard benchmark problem.

3. Result and Discussion

All the outputs were obtained using a concentration pulse input for 160 seconds with an initial concentration (Co) of 0.05 mg/l and a total simulation length of 1500 seconds. The BTCs are displayed at a location 8 cm from the initial source point of the pulse input. By changing the values of the parameters (K_f and a), a trend analysis for the BTCs (C/Co vs simulation time) for three alternative sets of parameters is generated with the help of MS Excel. Here; C/Co = aqueous phase relative concentration.

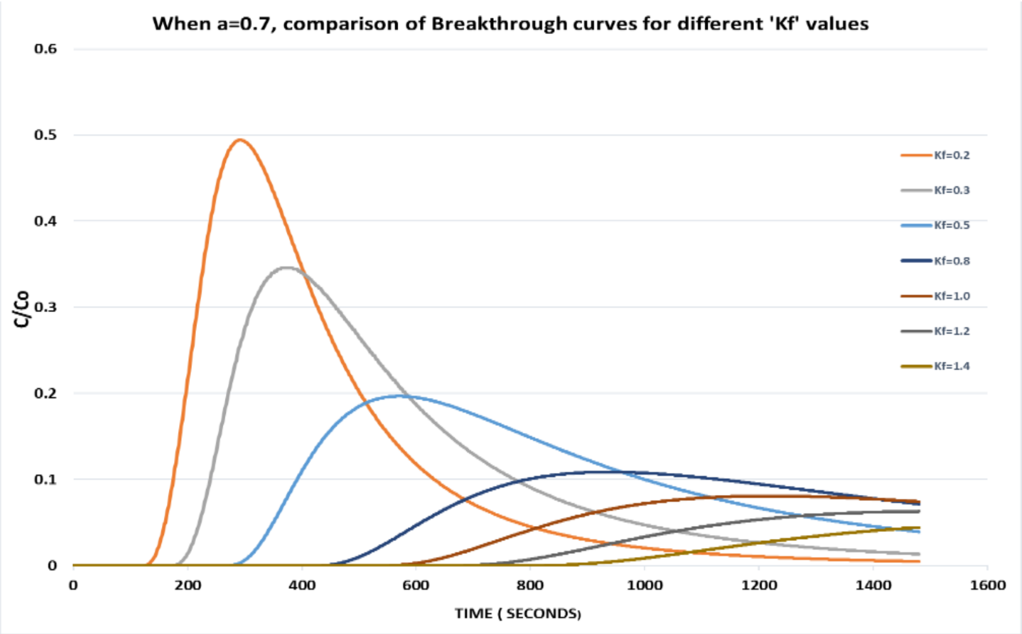

Figure 1: - when, a= 0.7, comparison of breakthrough curves for different K_f values.

It is being observed that with the same adsorption intensity (a), as the value of adsorption capacity increases, there is an attenuation in the peak of relative phase aqueous concentration since retardation to contaminants is offered by the solid phase (figure 2).

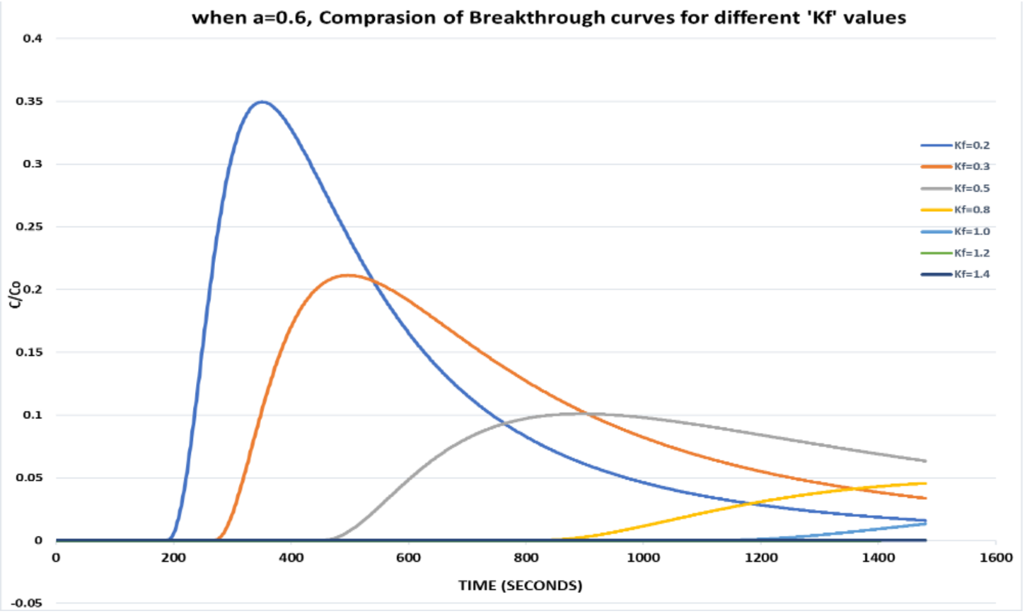

Figure 3: - when, a= 0.6, comparison of breakthrough curves for different K_f values

With a lower value of a= 0.6 and varying K_f, it is observed that the relative phase aqueous concentration drastically reduces and the peak is also delayed for each set since more resistance is offered to the contaminant (figure 4).

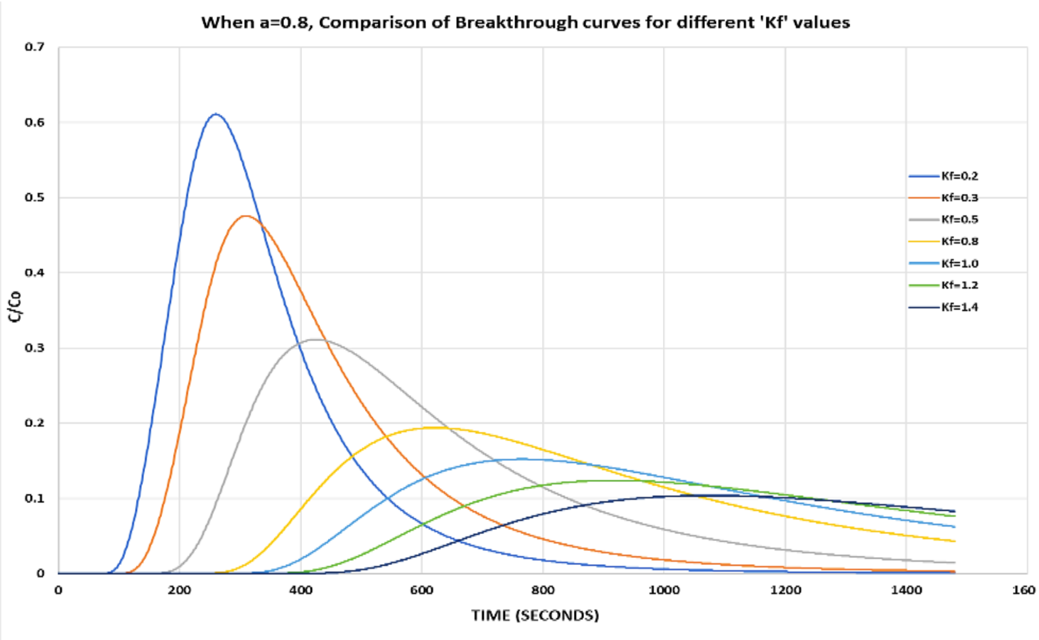

Figure 5: - when, a= 0.8, comparison of breakthrough curves for different K_f values.

With a higher value of a= 0.8 and by varying K_f, it is observed that the relative phase aqueous concentration is increased and the peak occurs earlier as compared to previous results (figure 6).

Also, it has been absorbed that at the same ‘a’ value and with an increase in K_f the peak is delayed and attenuated (aqueous phase relative concentration decreases with an increase in K_f).

4. Conclusion

A porous medium’s ability to adsorb contaminants from an aqueous solution is directly proportional to its adsorption capacity. As a result, the concentration of contaminants in the aqueous phase decreases when the adsorption capacity of the porous medium is higher, since more of the contaminant is adsorbed onto the solid phase. This leads to a reduction in the peak relative aqueous phase concentration and a slower rate of pollutant migration. However, a higher adsorption intensity can have an adverse effect on pollution migration. When the adsorption intensity is high, the concentration of contaminants in the aqueous phase increases compared to the concentration at a lower adsorption intensity, even when the adsorption capacity is the same. These critical parameters can be used to design a customized media with a suitable pollution removal process to treat targeted pollution.

Supplementary Materials: Not applicable.

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References

[1] A. Alam and A. Singh, “Groundwater quality evaluation using statistical approach and water quality index in Aurangabad,” *Rasayan J. Chem*. **2022**, 188, 180–188

[2] A. Alam and S. Kumar, “Groundwater Quality Assessment and Evaluation of Scaling and Corrosiveness Potential of Drinking Water Samples †,” *Environ. Sci. Proc.* **2023**, 25, 64-70

[3] C. Fetter, *Contaminant hydrogeology*. New york: Macmillan Publishing Company, **1993**.

[4] C. R. Fitts, “11 - Groundwater Contamination,” C. R. B. T.-G. S. (Second E. Fitts, Ed. Boston: Academic Press, **2013**, 499–585.

[5] P. Agarwal and P. K. Sharma, “Analysis of critical parameters of flow and solute transport in porous media,” *Water Sci. Technol. Water Supply*. **2020**, 20, 3449–3463

[6] T. S. Alomar, M. A. Habila, Z. A. Alothman, and N. Almasoud, “Evaluation of Groundwater and Grey Water Contamination with Heavy Metals and Their Adsorptive Remediation Using Renewable Carbon from a Mixed-Waste Source,” **2020**, 1–12

[7] D. B. Grove and K. G. Stollenwerk, “Computer model of one-dimensional equilibrium controlled sorption processes,” **1984**.

[8] C. Zheng, M. C. Hill, G. Cao, and R. Ma, “MT3DMS: Model use, calibration, and validation,” *Trans. ASABE*, **2012**, 55, 1549–1559

[9] M. M. Rahman, R. Liedl, and P. Grathwohl, “Sorption kinetics during macropore transport of organic contaminants in soils : Laboratory experiments and analytical modeling,” **2004**, 40, 1–11,

[10] Ajwa, Husein, William J. Ntow, Ruijun Qin, and Suduan Gao, "Properties of soil fumigants and their fate in the environment." *Hayes' Handbook of Pesticide Toxicology*. Academic Press, **2010**, 315-330.

[11] J. C. Igwe and A. A. Abia, “Adsorption isotherm studies of Cd (II), Pb (II) and Zn (II) ions bioremediation from aqueous solution using unmodified and EDTA-modified maize cob,” **2007**, 32, 33–42

[12] C. M. Chang, M. K. Wang, T. W. Chang, C. Lin, and Y. R. Chen, “Transport modeling of copper and cadmium with linear and nonlinear retardation factors,” *Chemosphere*, **2001,** 43, 1133–1139

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