

Groundwater Contaminant Transport FDM Modelling for Non-linear Freundlich and Langmuir Sorption with an Instantaneous Spill

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Abstract - Groundwater management is very necessary due to scarcity of surface water sources and has heavy stress on its utilization for different purposes. Contamination of water either on surface or in ground is crucial problem. Now days various models are developed to assess groundwater quality. When the contaminant is subject to chemical constituent that follows a non-linear sorption isotherm, the resulting differential equation is non-linear. Analytical solution of non-linear differential equation is difficult. In present paper, main focuses have been made on sorption of contaminant species in groundwater. Finite difference models were developed to assess the groundwater quality for different sorption isotherms namely, Freundlich and Langmuir with linear and non linear conditions. Results of numerical model were compared with available analytical model. It is found that all results are comparable and matches approximately. A combined study for plumes behavior for sorption and no sorption situations has carried out for spatial and temporal variation. Such kind of study would be useful for finding contaminant species interactions with groundwater when it subject to sorption for wide range of field conditions with regard to dispersion and source definition.

Keywords - Groundwater Modelling, Sorption Isotherm, Freundlichs, Langmuir, Finite Difference Model

I. Introduction

Management of groundwater resources including both quantity and quality requires the ability to establish a regional groundwater balance. Also quantum of flow of groundwater requires to predict water regimes in aquifers. Quality of groundwater depends up on many parameters like rate of groundwater flow, type of soil, porosity, hydraulic head, type of contaminant species. Information between and beyond monitoring locations and in the future are needed to understand the site and make informed decisions. Numerical modelling is an important aspect to integrate combine impact of all these parameters. In present paper one dimensional finite difference model were developed for forecasting of contaminant propagation under non-linearity in laboratory or field investigations at early or prolonged times after the spill. The practical scenario of an instantaneous spill has been studied for situations of non-linear Freundlich isotherm, and non-linear

Langmuir isotherm. All results were compared with established available analytical model. The developed numerical model can be used for the forecasting of contaminant dispersion in laboratory and field under non-linear reactions, or for the quantitative description of the effect of non-linearity in the sorption parameters, on the time-space distribution of the contaminant.

The finite difference method is a well known numerical method that has been applied to advection dispersion equation (Akram et al. 1999). The concept of linear "caricature" isotherm and its usefulness in obtaining exact analytical solutions were introduced for concentration profiles under nonequilibrium conditions (Manorajan 1995). An analytical solution for solute diffusion in a semi-infinite two-layer porous medium for arbitrary boundary and initial conditions obtained by Liu and Ball (1998) using the Green's function approach. An improved FDM has been developed by Hossain and Yonge (1999) to provide oscillation free results with the introduction of minimum artificial dispersion. A one-dimensional theory of contaminant migration through a saturated deforming porous media is developed by Smith (2000) based on a small and large strain analysis of a consolidating soil and conservation of contaminant mass. Analytical one-dimensional solutions are obtained by Pang and Hunt (2001) for continuous and pulse contaminant sources in a semi-infinite saturated porous medium when the dispersion coefficient increases linearly with distance downstream. Serrano (2001) used the method of decomposition for obtained series of solutions for the non-linear equation of advection and diffusion. These expressions permit an accurate forecasting of contaminant propagation under non-linearity in laboratory or field investigations at early or prolonged times after the spill. This paper presents the practical scenario of an instantaneous spill, and that of a constant concentration boundary condition for situations of non-linear decay, non-linear Freundlich isotherm, and non-linear Langmuir isotherm. Khebchareon and Saenton (2005) present an initial development of a one-dimensional numerical solution of mass transfer behavior of the entrapped dense non-aqueous phase liquid (DNAPL) in the subsurface environment where the system of equations is solved implicitly.

Many analysts worked on the non linearity problem of decay and sorption. But number of analyst considered only one or two parameter of non linearity in there model either in analytical or

numerical. In this model proposed combine effect of decay and sorption on account for the solution of governing equation of contaminant transport.

II. Contaminant Transport Mechanisms

There are three main physical processes effecting contaminant transport namely advection, dispersion and diffusion. In addition, chemical processes that effect transport are decay and sorption. Advection is the mass transport caused by the bulk movement of flowing ground water. The driving force is the hydraulic gradient. In highly permeable materials such as sand and gravel, advection is the most important transport process, and each transport prediction will only be as accurate as the flow description. Advective flow becomes more complex when the density and/or the viscosity of water change with solute concentration. Diffusion is the net flux of the solutes from a zone of higher concentration to a zone of lower concentration.

Diffusion over geological time, however, can have a significant impact. The effect of diffusion will normally be masked by the effect of advection in groundwater zones with high flow velocities. Dispersive spreading, within and transverse to, the main flow direction causes a gradual dilution of the contamination plume. Dispersive spreading will lead to increase in plume uniformity with travel distance. The combination of dispersion and diffusion termed as hydrodynamic dispersion. Degradation process also decreases the source of contamination with time. Reactions of the first order are applied to describe radioactive decay or simple degradation processes. Reactions of the first order are a linear and do not change the characteristics of the transport equation. Sorption refers to adsorption and desorption. Adsorption describes the adhesion of molecules or ions to the grain surface in the aquifer. The release from the solid phase is called desorption. Adsorption causes diminution of concentrations in the aqueous phase and a retardation of contaminant transport compared to water movement. The degree of sorption depends on a number of factors, including the concentration and the characteristics of the contaminant, the soil type and its composition, the pH value of water, and the presence of other water solutes. These factors are in time and space, resulting in a variation of retardation in the natural environment. The rate of adsorption onto the solid material as related to the concentration in the groundwater is expressed by adsorption kinetics. The relationship between the concentration of a solute in adsorbed phase and in the adjacent water phase at equilibrium is an adsorption isotherm (C.W. Fetter, 1993 and F.W. Schwartz, 1988).

III. Governing equation for contaminant transport

Assumptions taken in to considerations in model development are that the soil is homogeneous and isotropic, the porosity of soil is constant, saturated hydraulic conductivity is constant, ground water pore velocity is constant, one-dimensional flow is taken, hydrodynamic dispersion coefficient is constant, Freundlich and Langmuir parameters are constant and retardation factor is constant.

The one-dimensional advective-dispersive equations in an infinite aquifer subject to a general non-linear Freundlich isotherm of the form (Fetter, 1993)

$$\frac{\partial C}{\partial t} - D \frac{\partial^2 C}{\partial x^2} + u \frac{\partial C}{\partial x} + r b C^{b-1} \frac{\partial C}{\partial t} = 0 \quad -\infty < x < \infty, 0 < t \quad (1)$$

$$C(\pm\infty, t) = 0$$

$$\text{Where, } r = \frac{\rho_b K_f}{n}$$

The one-dimensional advective-dispersive equations in an infinite aquifer subject to a general non-linear Freundlich isotherm of the form (Fetter, 1993)

$$\frac{\partial C}{\partial t} - D \frac{\partial^2 C}{\partial x^2} + u \frac{\partial C}{\partial x} + \frac{r_1}{(1+\alpha C)^2} \frac{\partial C}{\partial t} = 0 \quad -\infty < x < \infty, 0 < t \quad (2)$$

$$C(\pm\infty, t) = 0$$

$$\text{Where, } r_1 = \frac{\rho_b \beta C}{n}$$

IV. Analytical solution for contaminant species transport under non linear freundlich sorption isotherm

Consider the case of contaminant dispersion in a long aquifer subject to a general non-linear Freundlich isotherm of the form (Fetter, 1993)

$$C_s = K_F C^b \quad (3)$$

If $b=1$, $K_F = K_d$ the linear distribution coefficient. Equation (1) becomes

$$\frac{\partial C}{\partial t} - D \frac{\partial^2 C}{\partial x^2} + u \frac{\partial C}{\partial x} + r b C^{b-1} \frac{\partial C}{\partial t} = 0 \quad (4)$$

$$\text{Where, } r = \frac{\rho_b K_f}{n}$$

As before, we write equation (4) as

$$C = C_0 - r b L_{x,t}^{-1} N C, \quad N C = C^{b-1} \frac{\partial C}{\partial t} \quad (5)$$

From equations (5), the second term in the decomposition series is

$$C_1 = -r b \int_0^t J_{t-\tau} C_0^{b-1} \frac{\partial C_0}{\partial \tau} \partial \tau \quad (6)$$

The equation (6) by Volterra integral yields as

$$C_1 = r b C_0^b \left\{ \frac{t(x-ut)^2}{2D(b-4)} - \frac{2t}{(b-2)(b-4)} + \frac{ut(x-ut)}{D(b-4)} - \frac{1}{(b-2)} \right\} \quad (7)$$

Higher-order terms in the series are obtained in a similar manner. As in the previous section, we used the concept of double decomposition in conjunction with the t-partial solution to arrive at a closed-form analytic simulant of the form

$$\left. \begin{aligned}
 C &\approx \frac{C_i e^{-\left[\frac{(x-ut\phi(x,t))^2}{4D\phi(x,t)}\right]}}{\sqrt{4\pi D\phi(t)}}, \quad C_i \gg 1 \\
 \phi(x,t) &= \frac{t}{(1+rbC_o(ut,t)^{b-1})\psi(x,t)^{b-1}}, \\
 \psi(x,t) &= \frac{1}{2} \operatorname{erfc}\left(\frac{x-ut}{\sqrt{4Dt}}\right) + \frac{e^{ux/D}}{2} \operatorname{erfc}\left(\frac{x+ut}{\sqrt{4Dt}}\right)
 \end{aligned} \right\} \quad (8)$$

C_o and ψ may be evaluated at $x=ut$, which sometimes produces a better agreement with other (numerical) solutions. In such case $\phi(t)$ is a function of t only, above equation is dimensionally consistent, since rbC_o and ψ are dimensionless.

For the case of no sorption, $b=0$ and for the case of linear sorption, $b=1$ and $\phi(t)$ becomes t/R , where $R = 1 + rb$ the retardation factor of linear sorption.

Now, the comparison with respect to the non linear series solution, extensive numerical experimentation indicated that equation (8) is virtually undistinguishable from the general decomposition series calculated for parameter values that assure its uniform convergence.

An important application in laboratory tests designed for parameter estimation, is the case of long-column experiments with constant source boundary condition. In this case, an analysis similar to the above leads to an analytic simulant of the form

$$C \approx \frac{C_i}{2} \left\{ \operatorname{erfc}\left(\frac{x-u\phi(t)}{\sqrt{4D\phi(t)}}\right) + e^{ux/D} \operatorname{erfc}\left(\frac{x+u\phi(t)}{\sqrt{4D\phi(t)}}\right) \right\}, \quad (9)$$

$$0 \leq x < \infty, \quad C_i \gg 1$$

where C_i = the concentration at the boundary, and $\phi(x,t)$ as in equation (8).

V. Analytical solution for contaminant species transport under non linear Langmuir sorption isotherm

Consider now the case of contaminant dispersion in a long aquifer subject to a non-linear Langmuir isotherm of the form (Fetter, 1993)

$$C_s = \frac{\alpha\beta C}{1+\alpha C} \quad (10)$$

The transport equation becomes

$$\frac{\partial C}{\partial t} - D \frac{\partial^2 C}{\partial x^2} + u \frac{\partial C}{\partial x} + \frac{r_1}{(1+\alpha C)^2} \frac{\partial C}{\partial t} = 0, \quad (11)$$

$$\text{Where, } r_1 = \frac{\rho_b \beta C}{n}$$

Equation (11) was subjected to the same analysis as described in the previous sections. Ultimately the analytic simulant, one arrives at equations (8) and (9), for instantaneous spill and constant source boundary condition, respectively. However, the function $\phi(x)$ now has the form

$$\phi(x,t) = \int_0^1 \frac{(1+\alpha C_o(x,t))^2}{(1+\alpha C_o(x,t))^2 + r_1} dt \quad (12)$$

Where, $C_o(x,t)$; this is the first solution in the decomposition series for an instantaneous spill, and constant source boundary condition $\phi(t) = t$. An analytical solution of this integral is difficult and a numerical solution is needed. However, in situations of mild non-linearity an approximation of equation (12) is possible.

Specifically,

$$\phi(x,t) \approx \frac{1}{1+r_1} \{t + 2\alpha i_1(x,t) + \alpha^2 i_2(x,t)\}, \quad (13)$$

$$\frac{\alpha C_i}{10} \leq 1$$

Where,

$$i_1(x,t) = \frac{C_i}{2u} \left\{ 1 - e^{-(ux/D)} + e^{(ux/D)} \operatorname{erf}\left(\frac{x+ut}{\sqrt{4Dt}}\right) - \operatorname{erf}\left(\frac{x-ut}{\sqrt{4Dt}}\right) \right\} \quad (14)$$

and

$$i_2(x,t) = \frac{C_i^2}{4\pi D} e^{-\left(\frac{(x-ut)^2 - x^2 e^{(ux/D)}}{2Dt}\right)} E_i\left(\frac{x^2 e^{(ux/D)}}{2Dt}\right) \quad (15)$$

An interesting feature of the Langmuir model is that α is a shape, or non-linearity, parameter, whereas β is a scale parameter. Unlike the Freundlich model, where the dimensions of K_F depend on b , the two parameters of the Langmuir model are not dimensionally related. Therefore, the latter allows us to explore the quantitative effect of non-linearity on the contaminant distribution in an aquifer.

The initial condition is exaggerated here to emphasize the differences between linear and non-linear effects, since our approximation (12) is limited to mild non linearities.

VI. Governing equation for contaminant transport

(a) The one-dimensional advective-dispersive equations in an infinite aquifer subject to a general non-linear sorption isotherm of the form

$$R_d \frac{\partial C}{\partial t} - D \frac{\partial^2 C}{\partial x^2} + u \frac{\partial C}{\partial x} = 0 \quad -\infty < x < \infty, 0 < t$$

$$C(\pm\infty, t) = 0$$

Where, R_d is retardation factor

(i) Freundlich retardation factor by Freundlich sorption isotherm

$$F = C_s = K_F C^b$$

Partition or Distribution coefficient $K_p = \frac{dF}{dC}$

$$\frac{dF}{dC} = K_F b C^{b-1}$$

$$R_d = 1 + \frac{\rho_b}{\theta} [K_F b C^{b-1}]$$

(ii) Langmuir retardation factor by Langmuir sorption isotherm

$$F = C_s = \frac{\alpha\beta C}{1 + \alpha C}$$

Partition or Distribution coefficient $K_p = \frac{dF}{dC}$

$$K_p = \frac{dF}{dC} = \frac{\alpha\beta(1 + \alpha C) - \alpha\beta\alpha C}{(1 + \alpha C)^2}$$

$$K_p = \frac{dF}{dC} = \frac{\alpha\beta}{(1 + \alpha C)^2}$$

$$R_d = 1 + \frac{\rho_b}{\theta} \left[\frac{\alpha\beta}{(1 + \alpha C)^2} \right]$$

VII. Solution of governing equation

Following assumptions are used for developing numerical model of contaminant transport equation:

- (1) The porous medium is homogeneous and isotropic.
- (2) The solute transport, across any fixed plane, due to microscopic velocity variations in the flow tubes, may be quantitatively expressed as the product of dispersion coefficient and the concentration gradient.
- (3) The flow in the medium is unidirectional and the average velocity is taken to be constant throughout the length of the flow field.
- (4) The FDM is approximations the higher order terms in Taylor's Series are neglected.
- (5) Contaminant is conservative i.e. decay is not considered for sorption cases. Also contaminant is assumed to be non reactive.
- (6) Contaminant is non conservative i.e. decay is considered in case of decay and combine effect of decay and sorption. Also contaminant is assumed to be non reactive.
- (7) Retardation process is considered in sorption cases.
- (8) No other process like pumping, recharge etc. is considered.

VIII. Numerical solution for sorbing contaminant species transport model

The one-dimensional advective-dispersive equations in a semi infinite aquifer subject to a general non-linear sorption isotherm of the form

$$R_d \frac{\partial C}{\partial t} - D \frac{\partial^2 C}{\partial x^2} + u \frac{\partial C}{\partial x} = 0 \quad (16)$$

The above equation may be solved for a variety of boundary and initial conditions. However, the following boundary and initial conditions were considered.

B.C. $C(x=0, t > 0) = C_0$ and $C(x=L, t \geq 0) = 0$

I.C. $C(0 < x \leq L, t = 0) = 0$

Equation (16) can be discretized as follows by employing second-order accurate central difference approximation of the advective term:

$$\frac{\partial C}{\partial t} = \frac{C_i^j - C_i^{j-1}}{\Delta t}$$

$$\frac{\partial C}{\partial x} = \frac{C_{i+1}^j - C_{i-1}^j}{2\Delta x}$$

$$\frac{\partial^2 C}{\partial x^2} = \frac{C_{i+1}^j - 2C_i^j + C_{i-1}^j}{\Delta x^2}$$

Where C_i^j is contaminant concentration at i-th space step and j-th step, Δx is space step and Δt is time step.

So the 1-D advection-dispersion equation becomes, in FDM form:

$$R_d \left[\frac{C_i^j - C_i^{j-1}}{\Delta t} \right] = D \left[\frac{C_{i+1}^j - 2C_i^j + C_{i-1}^j}{\Delta x^2} \right] - u \left[\frac{C_{i+1}^j - C_{i-1}^j}{2\Delta x} \right]$$

$$C_i^j - C_i^{j-1} = \frac{D\Delta t}{R_d\Delta x^2} (C_{i+1}^j - 2C_i^j + C_{i-1}^j) - \frac{u\Delta t}{2R_d\Delta x} (C_{i+1}^j - C_{i-1}^j)$$

$$C_i^j - \frac{D\Delta t}{R_d\Delta x^2} (C_{i+1}^j - 2C_i^j + C_{i-1}^j) + \frac{u\Delta t}{2R_d\Delta x} (C_{i+1}^j - C_{i-1}^j) = C_i^{j-1}$$

$$C_i^j - \frac{D\Delta t}{R_d\Delta x^2} C_{i+1}^j + \frac{D\Delta t}{R_d\Delta x^2} 2C_i^j - \frac{D\Delta t}{R_d\Delta x^2} C_{i-1}^j + \frac{u\Delta t}{2R_d\Delta x} C_{i+1}^j - \frac{u\Delta t}{2R_d\Delta x} C_{i-1}^j = C_i^{j-1}$$

$$-\frac{u\Delta t}{2R_d\Delta x} C_{i-1}^j - \frac{D\Delta t}{R_d\Delta x^2} C_{i-1}^j + (C_i^j) + \frac{D\Delta t}{R_d\Delta x^2} 2C_i^j + \frac{u\Delta t}{2R_d\Delta x} C_{i+1}^j - \frac{D\Delta t}{R_d\Delta x^2} C_{i+1}^j = C_i^{j-1}$$

$$\left(-\frac{u\Delta t}{2R_d\Delta x} - \frac{D\Delta t}{R_d\Delta x^2} \right) C_{i-1}^j + \left(1 + 2\frac{D\Delta t}{R_d\Delta x^2} \right) C_i^j + \left(\frac{u\Delta t}{2R_d\Delta x} - \frac{D\Delta t}{R_d\Delta x^2} \right) C_{i+1}^j = C_i^{j-1}$$

Let $\frac{u\Delta t}{2R_d\Delta x} = k1$, $\frac{D\Delta t}{R_d\Delta x^2} = k2$

So we have

$$(-k1 - k2) C_{i-1}^j + (1 + 2k2) C_i^j + (k1 - k2) C_{i+1}^j = C_i^{j-1}$$

$$P * C_{i-1}^j + Q * C_i^j + R * C_{i+1}^j = C_i^{j-1}$$

Where $P = (-k1 - k2)$, $Q = (1 + 2k2)$ and $R = (k1 - k2)$

Where i ranges from 2 to (n-1) [excluding the boundaries $x = 0$ and $x = n\Delta x$].

In matrix

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & \dots & 0 & 0 & 0 & 0 & 0 & 0 \\ (-k1-k2) & (1+2k2) & (k1-k2) & 0 & 0 & 0 & \dots & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & (-k1-k2) & (1+2k2) & (k1-k2) & 0 & 0 & \dots & 0 & 0 & 0 & 0 & 0 & 0 \\ \dots & \dots \\ \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & \dots & 0 & 0 & (-k1-k2) & (1+2k2) & (k1-k2) & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \dots & 0 & 0 & (-k1-k2) & (1+2k2) & (k1-k2) & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \dots & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} C_1^j \\ C_2^j \\ C_3^j \\ \dots \\ \dots \\ C_{n-2}^j \\ C_{n-1}^j \\ C_n^j \end{bmatrix} = \begin{bmatrix} C_0^j \\ C_2^{j-1} \\ C_3^{j-1} \\ \dots \\ \dots \\ C_{n-2}^{j-1} \\ C_{n-1}^{j-1} \\ C_n^{j-1} \end{bmatrix}$$

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & \dots & 0 & 0 & 0 & 0 & 0 & 0 \\ P & Q & R & 0 & 0 & 0 & \dots & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & P & Q & R & 0 & 0 & \dots & 0 & 0 & 0 & 0 & 0 & 0 \\ \dots & \dots \\ \dots & \dots \\ 0 & 0 & 0 & 0 & 0 & 0 & \dots & 0 & 0 & P & Q & R & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \dots & 0 & 0 & 0 & P & Q & R \\ 0 & 0 & 0 & 0 & 0 & 0 & \dots & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} C_1^j \\ C_2^j \\ C_3^j \\ \dots \\ \dots \\ C_{n-2}^j \\ C_{n-1}^j \\ C_n^j \end{bmatrix} = \begin{bmatrix} C_0 \\ C_2^{j-1} \\ C_3^{j-1} \\ \dots \\ \dots \\ C_{n-2}^{j-1} \\ C_{n-1}^{j-1} \\ C_n^{j-1} \end{bmatrix}$$

$$[M^F][C^j] = [R^F]$$

The matrix $[M^F]$ is tridiagonal and is constant. At each time step, systems of equations are solved for concentrations at the nodes by forward and backward substitutions using Gauss Elimination Technique.

IX. Results and discussion

(A) For Non Linear Freundlich Sorption Isotherm

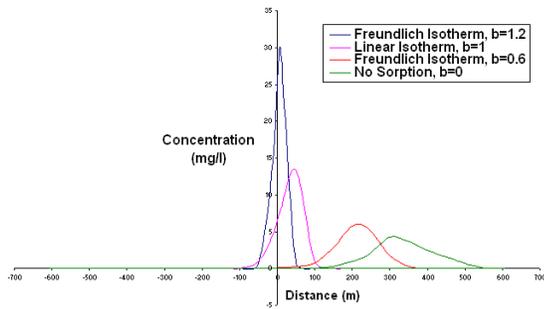


Fig. 1. Contaminant concentration distribution subject to a non-linear Freundlich isotherm sorption after an instantaneous spill for $b < 1$, $b = 0$, $b < 1$

Fig. 1. shows the concentration vs. distance profile. Again the comparison between linear ($R = 1 + rb$) and non-linear profiles is quantitative since the dimensions of K_F depend on b . Yet it is possible to see that the non-linear plume suffers retardation of the processes of advection and dispersion, but not as severe as that of the linear plume.

This retardation reduces the velocity of the plume center of mass and the plume variance, the degree of which is controlled by the magnitude of b .

It also shows that the non-linear plume suffers retardation of the processes of advection and dispersion that are more pronounced than that of the linear. This occurs because in this region of the isotherm the non-linear plume suffers more sorption than that of the linear plume. In the non-linear Freundlich sorption case the non-linear plume, indicating that the non-linear plume was more retarded than the linear.

It also shows the well-known phenomenon the non-linear plumes tend to be non-symmetric. Thus, equation (8) reproduces the well-known features of Freundlich sorption, namely the sharp leading edges and the “tailed” hind edges. Figure also shows the concentration spatial distribution in the absence of sorption according to equation (8); the concentration profile modeled by the solution to the transport equation subject to linear sorption (i.e., equation (8) with $\phi = t / (1 + r_1)$); and the concentration profile subject to Langmuir sorption according to equation (8) with ϕ given by equation (12).

(B) For Non Linear Langmuir Sorption Isotherm

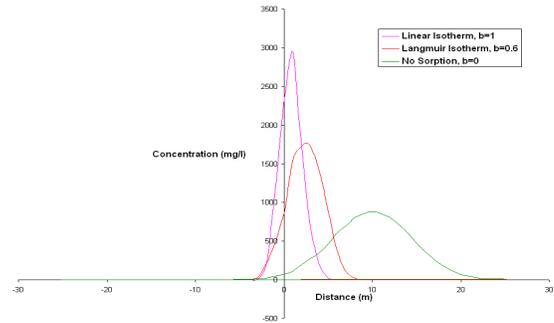


Fig. 2. Contaminant concentration distribution subject to a non-linear Langmuir isotherm after an instantaneous spill for $b < 1$, $b = 0$, $b < 1$ at 1 month

As explained before, each Langmuir parameter has dimensions independent of the magnitude of the other parameter. Thus, Fig. 2. indeed shows the quantitative effect of non-linearity on the shape of the plume. As expected, non-linearity causes a decrease in the velocity of the plume center of mass, and a corresponding increase in the magnitude of the maximum concentration with respect to the no sorption plume. This reduction in the center of mass, and corresponding increase in maximum concentration, is not as drastic as that of the linear plume.

The most “retarded”, or the least mobile, is the linear one, and the most mobile, or the most dispersive, is the one without sorption.

However, with the models introduced here, the hydrologist now has simple tools to evaluate quantitatively the effect of non-linearity.

(C) Comparison of analytical and numerical model

(i) For Non Linear Freundlich Sorption Isotherm

(a) For different time

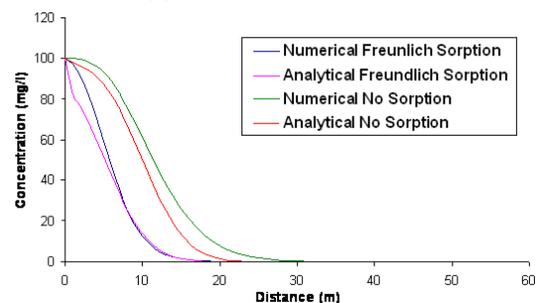


Fig. 3. Concentration Distribution at 10 month

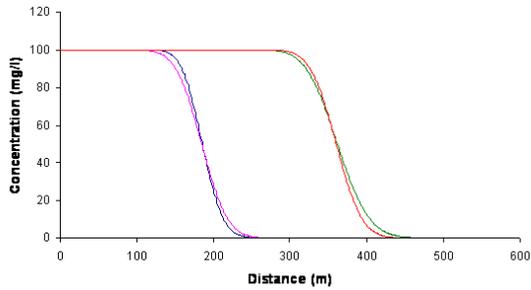


Fig. 4. Concentration Distribution at 120 month

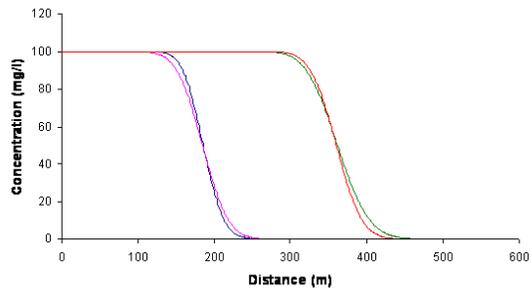


Fig. 5. Concentration Distribution at 360 month

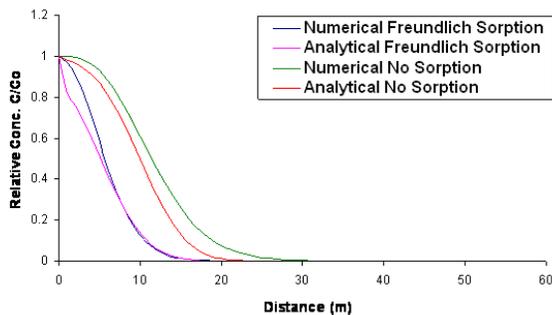


Fig. 6. Breakthrough at 10 month

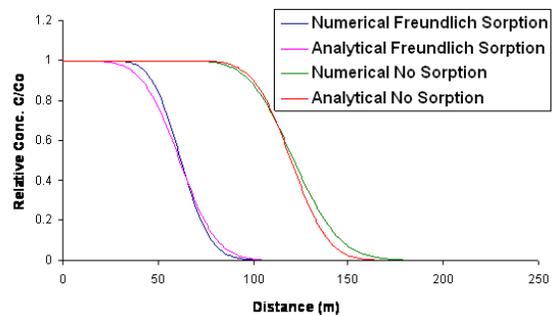


Fig. 7. Breakthrough at 120 month

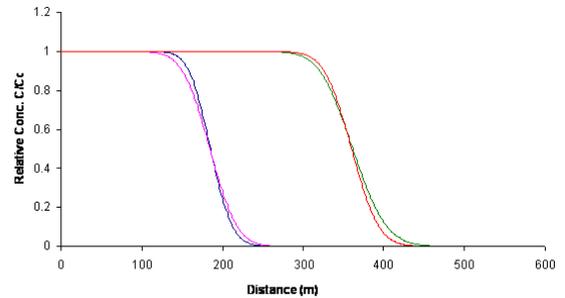


Fig. 8. Breakthrough at 360 month

Fig. 3, 4, and 5 are the plot of concentration distribution of contaminant species along the longitudinal movement of groundwater at different time. Fig. 6, 7 and 8 are the plot of relative concentration along longitudinal movement of groundwater at different time.

It is observed that plume of numerical model contaminant species move faster than analytical model contaminant species, shows that velocity of contaminant species due to sorption in numerical model is more than analytical model. Concentration reduces rapidly in case of numerical model than analytical model. Front of concentration distribution curve of numerical model is sharper than analytical model concentration distribution curve.

In case of no sorption nature of concentration distribution curve of analytical and numerical model is approximate same. Movement of plume in case of no sorption model is faster than plume of movement of sorption model because of velocity of contaminant species are not more affected.

(b) For different distance

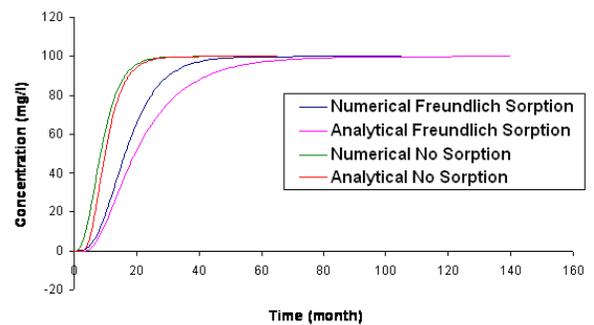


Fig. 9. Concentration Distribution at 10 meter

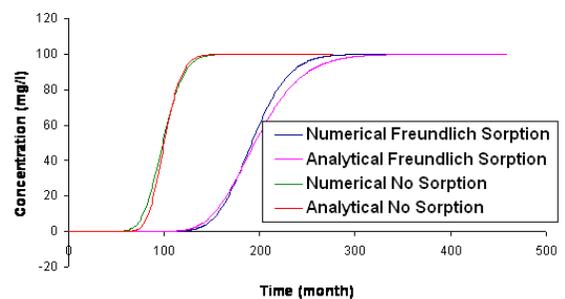


Fig. 10. Concentration Distribution at 100 meter

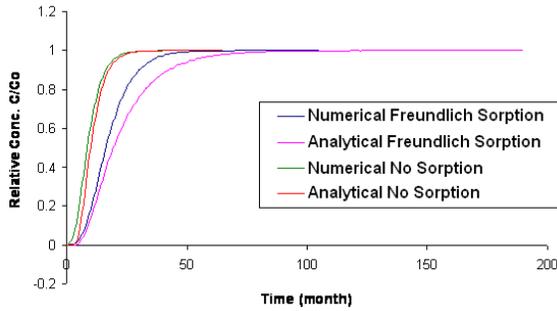


Fig. 11. Breakthrough at 10 meter

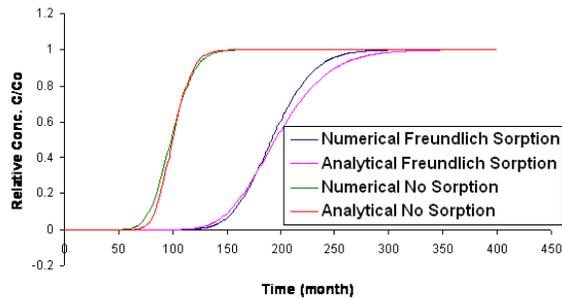


Fig. 12. Breakthrough at 100 meter

Fig. 9 and 10 are the plot of concentration distribution of contaminant species along the longitudinal movement of groundwater at different distances for different time. Fig. 11 and 12 are the plot of relative concentration along longitudinal movement of ground water at different distances for different time.

It is observed that plume of numerical model contaminant species move faster than analytical model contaminant species, shows that velocity of contaminant species due to sorption in numerical model is more than analytical model. Concentration reduces rapidly in case of numerical model than analytical model. Front of concentration distribution curve of numerical model is sharper than analytical model concentration distribution curve.

In case of no sorption nature of concentration distribution curve of analytical and numerical model is approximate same. Movement of plume in case of no sorption model is faster than plume of movement of sorption model because of velocity of contaminant species are not more affected.

(ii) For Non Linear Langmuir Sorption Isotherm
(a) For different time

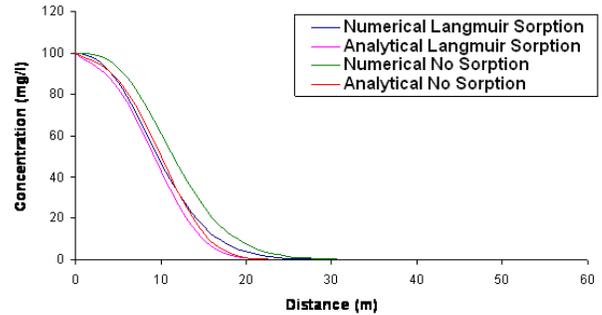


Fig. 13. Concentration Distribution at 10 month

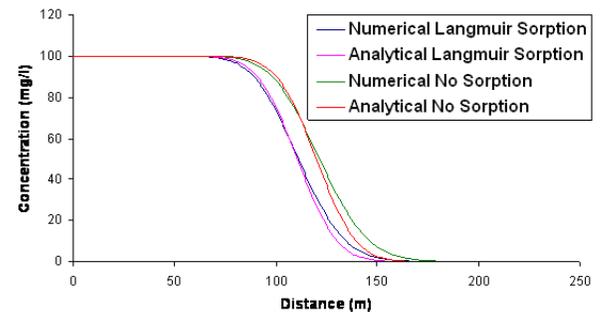


Fig. 14. Concentration Distribution at 120 month

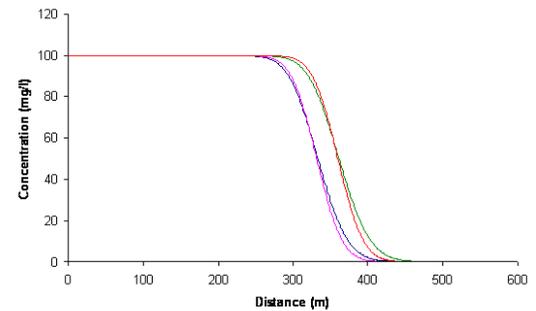


Fig. 15. Concentration Distribution at 360 month

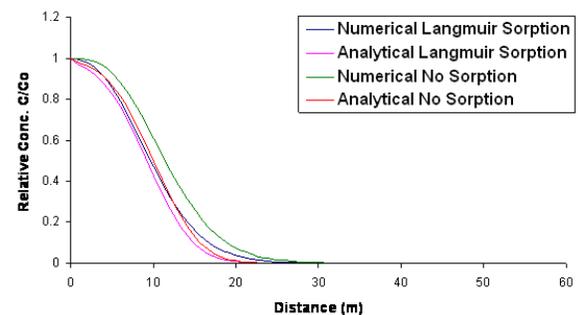


Fig. 16. Breakthrough at 10 month

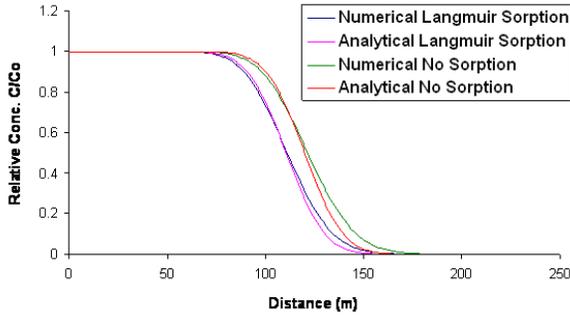


Fig. 17. Breakthrough at 120 month

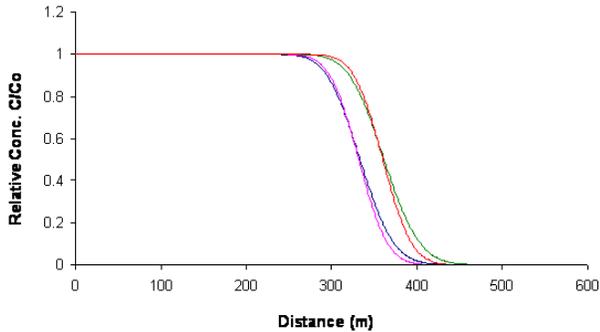


Fig. 18. Breakthrough at 360 month

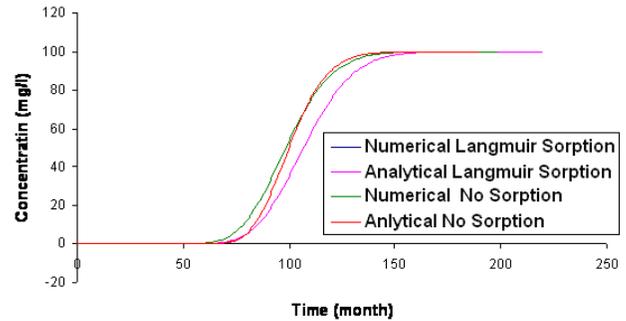


Fig. 20. Concentration Distribution at 100 meter

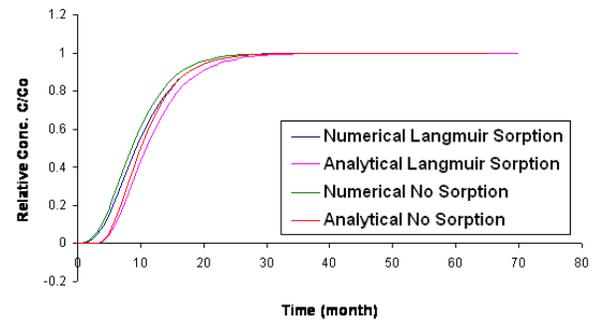


Fig. 21. Breakthrough at 10 meter

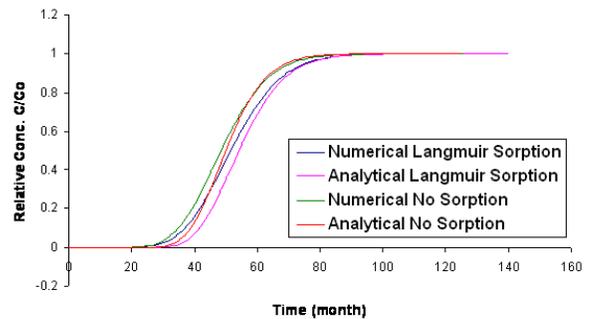


Fig. 22. Breakthrough at 100 meter

Fig. 13, 14 and 15 are the plot of concentration distribution of contaminant species along the longitudinal movement of groundwater at different time. Fig. 16, 17 and 18 are the plot of relative concentration along longitudinal movement of groundwater at different time.

It is observed that plume of numerical model contaminant species move little fast than analytical model contaminant species, shows that velocity of contaminant species due to sorption in numerical model is more than analytical model. Because of low value of Langmuir retardation parameter contaminant species velocity is not more affected and also behavior of sorption numerical and analytical model is same.

In case of no sorption nature of concentration distribution curve of analytical and numerical model is approximate same. Movement of plume in case of no sorption model is faster than plume of movement of sorption model because of velocity of contaminant species are not more affected.

(B) For different distance

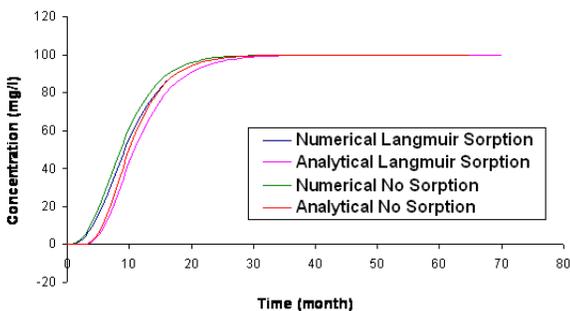


Fig. 19. Concentration Distribution at 10 meter

Fig. 19 and 20 are the plot of concentration distribution of contaminant species along the longitudinal movement of groundwater at different distances for different time. Fig. 21 and 22 are the plot of relative concentration along longitudinal movement of groundwater at different distances for different time.

It is observed that plume of numerical model contaminant species and analytical model contaminant species follow approximately same path, show that if all the hydraulic property of aquifer for the numerical and analytical model is same it gives approximately same results.

In case of no sorption nature of concentration distribution curve of analytical and numerical model is approximate same.

X. Conclusions and scope

A plume undergoing non-linear sorption according to a Freundlich isotherm retards the processes of advection and dispersion with respect to a plume with no sorption. Similar to the case of non-linear decay, whether this retardation is more or less pronounced than that of the linear sorption plume depends on whether the values of b greater or less than 1. When $b < 1$, the decrease in mobility in the non-linear plume is not as pronounced as that of a plume modeled by a linear isotherm. Plume shape may be quite sensitive to the values of the non-linear parameters. Plumes with parameter values $b < 1$ exhibit the well known lack of symmetry with respect to their center of mass, sharp fronts, and the tailing effects observed at hazardous waste sites. As the magnitude of the non-linear parameter increases, the non-linear plume approaches the linear one. This partial non-linear “retardation” can now be observed quantitatively with the models presented herein. The models developed also simulate the case of $b > 1$ (i.e., “unfavorable” sorption), which produce a plume even more retarded than the linear.

The shape of a contaminant plume following a non-linear Langmuir isotherm is very sensitive to the magnitude of the non-linear parameter a . For values of a tending to zero the plume modeled according to a Langmuir isotherm tends to coincide with that with no sorption. As the magnitude of a increases, the shape of the plume is affected by showing more sorption at lower concentrations.

However, the approximate analytical models presented here are not capable of predicting the form of a contaminant plume when the initial concentration is large and at the same time α is large, or when $\alpha > C_i$. More research is needed on the identification of simple solutions for the latter conditions.

The FDM predictions were found to be in excellent agreement with analytical solutions for a wide range of field conditions with regard to dispersion and source definition. The new developed numerical model can be used for the forecasting of contaminant dispersion under non-linear reactions, or for the quantitative description of the effect of non-linearity in the sorption parameters, on the time-space distribution of the contaminant. The solution for numerical values of state variable only at specified points in the space and time domains defined for the problem. The above FDM model solved by using implicit scheme is unconditionally stable. The proposed models are flexible, stable, and could be used for laboratory or field simulations at early or prolonged contamination scenarios. In this developed model groundwater velocity taken as a constant, we can develop another model using same methodology for groundwater flow velocity. The methodology developed can easily be extended to two or three-dimensional problems.

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