Fluoride Ion Leaching Kinetics in Soil: A Mechanistic Model

Poonam Soni[1], Arun Kumar[2], A. Rani[3]
[1]Assistant professor, [2]Associate professor, [3]Professor
[1,2,3] Department of Applied Mathematics
[1,2,3] Thadomal Shahani Engineering College, Mumbai, India

Abstract: Fluoride ion is a ubiquitous micro pollutant in groundwater and the risk for fluorosis associated with use of such water for human consumption is one of the environmental hazards faced worldwide. The aim of this paper is to present a mechanistic model for leaching kinetics of fluoride ion on undisturbed soil column. The mathematical formulation takes into account convective-transport, hydrodynamic dispersion and retardation factor. Appropriate initial and boundary conditions have been set as per the soil kinetics. The mechanistic model so developed is based on the assumption that flow in the soil column is in vertical direction and one dimensional only, soil profile is homogeneous and isotropic. Based on these assumptions the partial differential equations so obtained have been solved numerically using explicit finite difference method. The full model does seem capable of modelling the experimentally observed break-through curves but a much greater understanding of the underlying chemistry is required to develop a more refined model.

IndexTerms: Fluoride ion, explicit finite difference method, retardation factor, leaching kinetics.

I. INTRODUCTION

Mathematical modelling is the integral component of any effort to predict the migration and the persistence of pollutants to and within groundwater systems. The models are helpful tools to design and implement soil and crop management practises which minimize soil and water contamination.

The process of transport of reactive contaminants through porous media has been represented by various mathematical models over the years.Valocchi(1985)presented aquantitative criterion to assess the validity of the local equilibrium assumption for one-dimensional, steady flow through homogeneous soils.Goltz and Roberts (1986) have modelled the tailing of breakthrough responses, experimentally observed during flow through porous media, by dividing the porous medium into regions of mobile and immobile water, and coupling the advective‐dispersive solute transport equation with expressions to describe diffusional transfer between the two regions.Brusseau et al (1989) presented a model that explicitly accounted for multiple sources of nonequilibrium. The multiprocess nonequilibrium (MPNE) model was specifically formulated for cases where nonequilibrium is caused by a combination of transport- and sorption-related processes. Out of the numerous investigations conducted on the transport and persistence of contaminants in the soil system most of them have focussed more on the transport of parent material. Rao et al (1980) estimated retention of pesticides and transformation parameters required in non-point source contamination.Enfield et al (1982) developed three simplistic models are for evaluating the transport of organic pollutants through soil to ground water considering mobility and first‐order degradation. The first calculated linear sorption/desorption of the pollutant and first‐order degradation without considering dispersion. The second took dispersion also into account. The third model considered nonlinear sorption following a Freundlich equation and first‐order degradation but for dispersion. Zhong et al(1986)quantified pesticide adsorption and degradation during transport through soil to groundwater.

Fluoride occurs naturally in soils and rocks as calcium fluoride, cryolite and fluorapatite. It is an essential element required, though in small amount, for the skeletal and dental development of mammals. There has been a lot of controversy in recent years among the scientists regarding the beneficial and toxic effects of Fluoride as mentioned by John (1998).The Fluoride sorption by soil has been a topic of investigation by many researchers.Polomski (1982) studied the changes in soil brought about by contamination by fluoride. These changes also make alterations in soilsolution chemistry, particularly in pH and aluminium chemistry. Robbins (1986)studied fluoride adsorption by a saline sodic soil irrigated with a high fluoride water considering a Langmuir isotherm.

In order to understand the perils of fluoride contamination in soil and in groundwater it is important to investigate the movement characteristics of fluoride and its dynamic distribution. The transport rules of fluoride migration in soil and groundwater are determined by geo-chemical background, climatological factors, adsorption and leaching of fluoride in soil and groundwater. Wuyi et al (2002) studied the adsorption and leaching of fluoride in typical Chinese soils inrelation to physical and chemical parameters of the soils.The study showed that the adsorption of F in soils decreased from humid areas to arid areas and from acidic soils to alkaline soils. The smaller loss of F leachingoccurred from acid soil in tropical humid areas and in temperate semi-humidcompared with arid areas. The adsorption and leaching processes directly affect fluoride migration and exchange from soil to water.

An analytical solution of the reactive transport equation in a finite soil column for both continuous and pulse-type solutes at the soil surface has been developed.The analytical solutions for one-dimensional advection-dispersion transport in finite spatial domain subject to first- and third-type inlet boundary conditions were presented by Clearly and Adrian (1973), Selim and Mansell (1976), respectively. The solution of transport equation considered reversible and irreversible solute adsorptions. The irreversible adsorption was represented by the sink/source term.
The present paper proposes a mathematical model for leaching of Fluoride ion in soil in presence of excess / (potassium/sodium) ions, using the soil column experiment by Saxena and Rani (2012) in the laboratoryfor Alkaline Soils of Indian Origin.Potassium/Sodium Fluoride was use as a tracer through the soil column. The transport equations have been solved using explicit finite difference method and breakthrough curves have been obtained.

II.THEORETICAL DEVELOPMENT AND GOVERNING EQUATIONS

The soil column has been assumed to be a homogeneous and isotropic porous medium that is having same water content, bulk density and retention factor. Only the vertical steady-state flow of water perpendicular to the soil layer is investigated.

The governing one-dimensional advective–dispersive transport equation considering equilibrium sorption and first-order degradation constant of ion as observed in the soil column experiment can be written as

$$\frac{\partial\theta[F^-]}{\partial t}+\frac{\partial(\rho S)}{\partial t}=D\left\{\frac{\partial^2(\theta\,[F^-])}{\partial z^2}\right\}-q\frac{\partial[F^-]}{\partial z}-\theta k[F^-] \qquad (1)$$

Where $[F^-]=$ concentration of leached fluoride ion in the solution phase, S= concentration of the ion in the adsorbed phase, θ= volumetric water content; q= Darcy's Flux; k= first order degradation constant for fluoride ion, D= Dispersion coefficient,ρ =soil bulk density,z =is vertical coordinate measured vertically downwards, t = is time in sec.

For linear casewhere K=distribution coefficient for $[F^-]$ion and

$$\frac{\partial S}{\partial t}=K\frac{\partial[F^-]}{\partial t} \qquad (2)$$

Substituting the value of$\frac{\partial S}{\partial t}$equation (2) in equation (1) and simplifying we get the following expression

$$\left(\frac{\rho K}{\theta}+1\right)\frac{\partial[F^-]}{\partial t}=D\frac{\partial^2[F^-]}{\partial z^2}-\frac{q}{\theta}\frac{\partial[F^-]}{\partial z}-k[F^-] \qquad (3)$$

Or writing above equation (3) as

$$R\frac{\partial[F^-]}{\partial t}=D\frac{\partial^2[F^-]}{\partial z^2}-V\frac{\partial[F^-]}{\partial z}-k[F^-] \qquad (4)$$

Where, $R=1+\frac{\rho K}{\theta}$known as the RetardationFactor and $V=\frac{q}{\theta}$the pore water velocity.

The initial and boundary conditions applied to equation (4) are

$$[F^-]=[F^-]_i \quad when\, t=0,\ z\geq 0 \qquad 4(a)$$

$$[F^-]=\begin{cases}[F^-]_{ad} & 0<t\leq t_0\\ 0 & t>t_0\end{cases} \qquad 4(b)$$

$$\left.\frac{\partial[F^-]}{\partial z}\right|_{z=\infty}=0 \qquad 4(c)$$

Here $[F^-]_i$ is the leachable$[F^-]$ concentration present initially in the soil column and$[F^-]_{ad}$ is the $[F^-]$concentration introduced in the soil column and the pulse time is $t=t_0$.

Applying the explicit scheme of finite difference methodas by Majchrzakand Mochnacki(2004) to equation (4) and writing fluoride ion concentration at any time t as$C$ i.e.$[F^-]$the following approximation of the said equation (4) is obtained for an internal node i

$$R\frac{C_{i,j}-C_{i,j-1}}{\Delta t}=D\frac{C_{i-1,j-1}-2C_{i,j-1}+C_{i+1,j-1}}{\Delta z^2}-V\frac{C_{i+1,j-1}-C_{i-1,j-1}}{2\Delta z}-kC_{i,j} \qquad (5)$$

Simplifying equation (4) the following expression is obtained

$$\left[1+\frac{k\Delta t}{R}\right]C_{i,j}=C_{i,j-1}\left[1-\frac{2D\Delta t}{R\Delta z^2}\right]+C_{i-1,j-1}\left[\frac{D\Delta t}{R(\Delta z)^2}+\frac{V\Delta t}{2R\Delta z}\right]+C_{i+1,j-1}\left[\frac{D\Delta t}{R(\Delta z)^2}-\frac{V\Delta t}{2R\Delta z}\right] \qquad (6)$$

For equation (6) to be stable

$$\left[1-\frac{2D\Delta t}{R(\Delta z)^2}\right]\geq 1 \qquad and \quad \left[\frac{D\Delta t}{R(\Delta z)^2}-\frac{V\Delta t}{2R\Delta z}\right]\geq 0 \qquad (7)$$

Here i represent the number of nodes and j represents the time levels, Δz represents the grid size along travel distance and Δtrepresents the time interval.

The system of linear equations so obtained were solved using Gauss –Jordan Method. The values of Δz were taken in consonance with equation (7). The spatial$[F^-]$concentration profile for fluoride transport through the soil column has been shown in Fig.1.The numerical results of concentration profiles of $[F^-]$have been compared with experimental results and verified..

III.NUMERICAL RESULTS AND DISCUSSION OF USE

This section shows the results obtained numerically in the form of initial leaching rate profile for [F^-]leaching for added salt KF at the specified values of parameters given in the Table (1)below

Table 1: Values of some physio-chemical parameters of the soil Saxena and Rani (2012)

Symbol	Constant	Values
pH	Soil pH	8.2
ρ	Bulk Density	$1.48 gm/cm^3$
θ	Water filled porosity θ	$0.315 cm^3/cm^3$
k	First order degradation constant	$0.00414/sec$
V	Pore water velocity	$0.75 cm/sec$

The leaching profiles in Fig.1 represent the plotted graph between time and the [F^-]_lthat is leachable fluoride remaining at time t in the soil column. The numericalresults show good agreement with the experimental values. In the laboratory experiment by Saxena and Rani (2012) thefluoride source is supplied for predefined timet_0(24 hrs.), that is it has a finitepulse source. The pore volume and relative concentration profile for leached [F^-]concentrationFig.2 has been predicted for column Peclet numberP_e=2, Dispersion coefficientD=22.5 〖cm〗^2/sec ,and Retardation factorR=1.5.The column Peclet number is expressed asP_e=VL/D where V= pore velocity; L= column length= 60 cm; D= dispersion coefficient. From the graphs it is clear that numerical results are in good agreement with the experimental values.

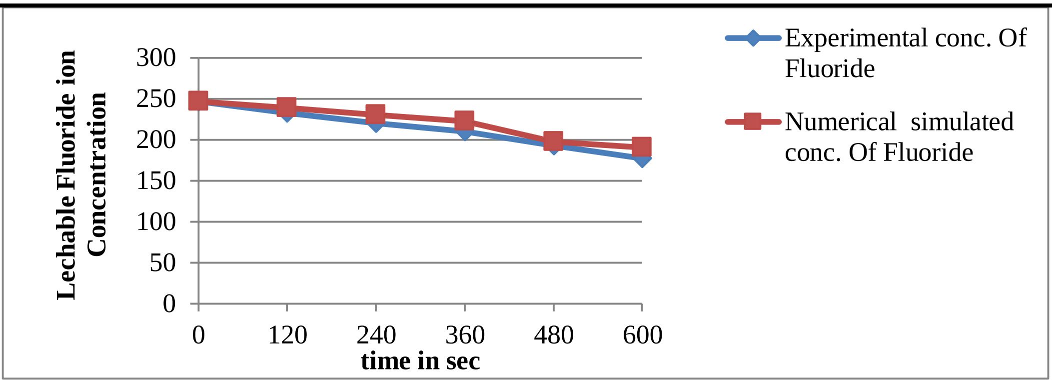

Fig.1 Leachable Fluoride ion concentration vs time

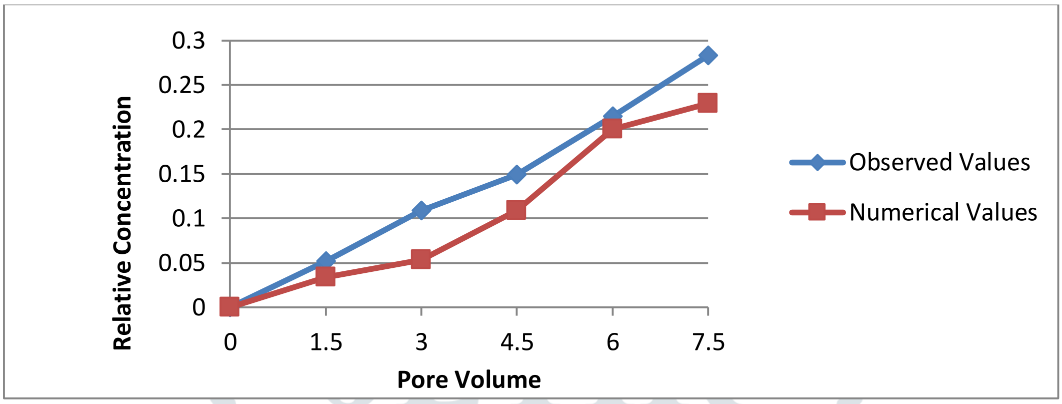

Fig.2 Pore Volume vs Relative Concentration of Leached Fluoride ion

IV. CONCLUSION:

Experimental and numerical results of BTCs have been presented for fluoride iontransport in soil. Numerical explicit finite-difference method was used to get the solution of advective–dispersive transport equation. The experimental BTCs fluoride ion through soil column has been simulated well by using the numerical model.This study indicates that the effect of pollutant fluoride ion is not uniform but decreases with time. Thepaper demonstrates that the combination of multicomponent chemistry, diffusion-limited sorption and transport can be modelled by combining mechanistic process descriptions. There were often more influencingfactors than initially anticipated, even in relatively simple systems and the present model provide for the inclusion and amendment for the same. Nevertheless, mechanistic modelling provides valuable insights into the processes that are involved in transport of fluoride in soil systems. The numerical simulation exhibits a good comparison of the observed and simulated values.

REFERENCES

[1] Brusseau H.L, Jessup R.E and Rao P.S.C.1989. Modeling the transport of solutes influenced by multi process non-equilibrium.Water Resour. Res.,25: 1971–1988.
[2] Clearly, R. W. and Adrian, D. D. 1973. Analytical solution of the convective-dispersive equation forcation adsorption in soils, Soil Sci. Soc. Am. Pro., 37, 197–199.
[3] Enfield, C.G., R. F. Carsel, S.Z. Cohen, T. Phan and D.M. Walters.1982. Approximating pollutant transport to ground water. Ground water.V. 20, pp. 711-722.
[4] Goltz, M.N and Roberts P.V. 1986. Three-dimensional solutions for solute transport in an infinite medium with mobile and immobile zones. Water Resour. Res.,22(7): 1139–1148.
[5] John, R. L., 1998. Earth Island J., Spl Rep., San Francisco, 7.
[6] Majchrzak, E. and Mochnacki, B. 2004. Numerical Methods. Theoretical Bases, Practical Aspects and Algorithms, Publ. of the Silesian University of Technology, Gliwice.
[7] Mochnacki B.and Suchy J.S. 1995. Numerical Methods in Computations of Foundry Processes, PFTA, Cracow.
[8] Polomski, J., Fuhler, H. and Blaser. 1982. Accumulation of airborne fluoride in soils.J.Enviorn.Qual., 11,457-461.
[9] Rao, P.S.C and J. M. Davidson. 1980. Estimation of pesticide retention and transformation parameters required in nonpoint source pollution models. In Environmental Impact of Nonpoint Source Pollution.Overcash, M.R., Davidson, J.M., Editors, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan.
[10]]Robbins, C.W. 1986.Fluoride adsorption by asaline sodic soil irrigated with a high fluoride water. Irrig.Sci,7,108-112.
[11] Saxena, S and Rani, A. 2012. Fluoride Ion Leaching Kinetics for Alkaline Soils of Indian Origin. Journal of Scientific Research and Reports, V.1. 29-40.
[12] Selim, H. M. and Mansell, R. S. 1976. Analytical solution of the equation for the transport of reactive solutes through soils, Water Resour. Res.,12, 528–532.
[13] Valocchi,A.J. 1985. Validity of the local equilibrium assumption for modeling sorbing solute transport through homogeneous soils. Water Resour. Res,21(6): 808–820.
[14] Wuyi W, Li R, Tan J, Luo K, Yang L, Li H and Li Y. 2002. Adsorption and leaching of fluoride in soils of China. Fluoride.35(2):122-129.
[15] Zhong, W.Z., Lemley, A. T. andWagnet. R. J. 1986. Quantifying pesticide adsorption and degradation during transport through soil to groundwater. In: Evaluation of pesticides in ground water.Garner, W. Y., Honeycutt, R. C. and Nigg, H. N.,Eds. ACS Symposium Series 315; American Chemical Society: Washington, DC.