Transport of Fluoride Ions in Soil Under Transient Flow Conditions: A Mathematical Approach

A Thesis

Submitted for the Award of Ph.D. degree of

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in the

Faculty of Science

By

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KOTA(RAJ.)
2019

Dedicated

To

My Father

Supervisor Certificate

I feel great pleasure in certifying that the thesis entitled **“Transport of Fluoride Ions in Soil Under Transient Flow Conditions: A Mathematical Approach”** submitted by **Poonam Soni** under my guidance.

She has completed the following requirements as per Ph.D. regulation of the University.

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ABSTRACT

The thesis contains seven chapters.The first chapter gives an introduction about the soil characteristics, its composition, genesis. The solute transport processes for the transport of contaminants in soil and basic mathematical equations governing the transport of contaminant in soil with different possible solution techniques have been discussed. The importance of fluoride as a micro-nutrient for mammals as well as its harmful effects if its presence exceeds a specified level has been discussed. Thus, the need for a mathematical model, with an underlying physical concept, to assess its transport in soil and as a result in groundwater is necessitated.

The second chapter is about the review of literature undertaken for a comprehensive understanding of fluoride in soil. The different fluoride producing sources and factors affecting its availability in soil have been studied. The literature study gives insight about the chemically reactive nature and complex migration processes of fluoride in soil.

The third chapter entitled Mathematical Formulation and Solution for Fluoride Ion Transport in Soil studies the fluoride transport process modelled on the soil water column experiment conducted in the laboratory. While developing the mathematical model 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. Also, the application of fluoride as a contaminant is considered to be pulse type as per the laboratory experimental conditions. The contaminant is considered as degrading type with first order degradation. The equation is solved analytically as well as numerically assuming pulse type boundary conditions with some initial concentration of fluoride already present in soil. The values of the parameters to be used are taken as used in soil column experiment. The results obtained both analytically and numerically for leachable fluoride

remaining at time t in the soil column at different values of added fluoride are represented graphically. The pore volume and relative concentration profile for leached fluoride concentration are also represented graphically.

The study of graphs shows that analytical results are more comparable to experimental results as compared to the numerical results. The numerical simulation also exhibits a fair comparison of the experimental and simulated values. The one-dimensional model provides valuable insights into the processes that are involved in transport of fluoride in soil systems.

In chapter 4, a two-dimensional model for fluoride transport in soil has been presented in which, the transverse component of velocity and dispersion coefficients are also considered along with the longitudinal components. The initial and pulse-type boundary conditions have been considered. The longitudinal and transverse seepage velocities have been taken to be constant. The properties of soil column experiment are extended to the two-dimensional model also and therefore in the model it is assumed that the soil medium to be homogeneous, isotropic saturated and of semi-infinite in horizontal plane. Since fluoride is reactive in nature and has the tendency to get adsorbed in the medium retardation factor and a first order decay term as a constant is also considered. Since, in the earlier chapter for one dimensional model, the analytical solution shows more comparison with observed experimental values, the solution for two-dimensional model is obtained analytically by employing Laplace Transform technique.

The concentration values of fluoride have been obtained from the analytical solution in the presence of initial fluoride concentration for a chosen set of numerical values of the different variables and represented graphically.

In Chapter 5 a one-dimensional advection diffusion mathematical model to assess the transport of fluoride in presence of chemical moieties present in soil environment has been presented. The transient flow of velocity has been considered exponential in one case and sinusoidal for another case. The solution of the model is obtained analytically and results obtained for leachable fluoride vs time have been plotted for steady state and transient state in presence of different hydroxides.

It has been observed that under transient flow conditions, for the exponential form of velocity, the leachable fluoride ion concentration decreases faster than in the sinusoidal form of velocity. The concentration levels for sinusoidal form of velocity are higher than that of exponential form of velocity. The analytical results obtained for steady state are in consonance with the experimental values and therefore offer good comparison. The model can be used to represent realistic conditions where field conditions are same as in the study.

Chapter 6 represents an attempt to model chemical ion transport through soil using Laplace Adomian Method. The effect of an external pressure / force in the form of gravitational force on flow through a porous medium has been studied by assuming the flow to be Newtonian. The chapter employs Laplace Adomian Decomposition Method to solve the equation for boundary layer flow of an incompressible fluid in the absence of pressure gradient. The study has been carried out for the flow in soil subject to external forces like gravity.

In chapter 7 future scope and prospects of the study have been discussed. The vadose zone is highly complex and is not a homogeneous and isotropic medium as considered in the study. The field situations are quite different from the laboratory conditions and therefore, the present model has its limitations in predicting confidently the presence of fluoride ion in a regional aquifer. Future works in developing a model for fluoride transport must include actual filed like situations. Also, the present mathematical model may be solved using different numerical schemes of finite difference and finite element or finite volume method and the results so obtained may be validated with the experimental or actual field like situations.

Candidate's Declaration

I, hereby, certify that the work, which is being presented in the thesis, entitled **"Transport of Fluoride Ions in Soil Under Transient Flow Conditions: A Mathematical Approach"** in partial fulfilment of the requirement for the award of the Degree of Doctor of Philosophy, carried under the supervision of Dr. Arun Kumar and submitted to the Department of Mathematics, Government College, Kota, University of Kota, Kota; represents my ideas in my own words and where others ideas or words have been included. I have adequately cited and referenced the original sources. The work presented in this thesis has not been submitted elsewhere for the award of any other degree or diploma from any Institutions. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will cause for disciplinary action by the University and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

Poonam Soni
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This is to certify that the above statement made by Poonam Soni (Enrolment No: ………………..) is correct to the best of my knowledge.

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Thesis Approval for Doctor of Philosophy

This thesis entitled **“Transport of Fluoride Ions in Soil Under Transient Flow Conditions: A Mathematical Approach”** by Poonam Soni, Registration No: RS/1830/16 submitted to the Department of Mathematics, Govt. College, Kota, Kota is approved for the award of degree of Doctor of Philosophy.

Examiners

Supervisor (s)

Chairman DRC

Date:

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Acknowledgement

“No one who achieves success does so without the help of others. The wise and confident acknowledge this help with gratitude.” – Alfred North Whitehead

At this point of submission of my thesis, which is the result of my sincere efforts, arduous research and perseverance, I would like to take this opportunity to express my heartfelt gratitude to all the people who helped me in the successful culmination of this study by guiding, assisting and supporting in the best possible manner.

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There are so many others whom I may have inadvertently left out, still I sincerely thank all of them for their help.

Kota (POONAM SONI)

The present thesis entitled **“Transport of Fluoride Ions in Soil Under Transient Flow Conditions: A Mathematical Approach”** consists of the following research papers: -

1. Arun Kumar, Poonam Soni and Ashu Rani **“Laplace Adomian Decomposition Method to study Chemical ion transport through soil”.** Appl. Appl. Math. (R1150_AAM_AK_051718 accepted August 4,2018.)
2. Poonam Soni, Arun Kumar, Ashu Rani **“Fluoride Ion Leaching Kinetics in Soil: A Mechanistic Model”** Journal of Engineering Technology and Innovative Research (JETIR), 2019, Vol.6, (3),135-137.

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Transport of Fluoride Ions in Soil Under Transient Flow Conditions: A Mathematical Approach

Chapter 1

Introduction

1.1 SOIL

“Soil is the unconsolidated mineral and organic matter on the surface that has been subjected to and influenced by genetic and environmental factors of parent material, climate (including moisture and temperature effects), macro-and microorganisms, topography, all acting over a period of time and producing a product – soil – that differs from the material from which it is derived in many physical chemical, biological and morphological properties and characteristics.” [1]. The basis of standard classification of soil into sand, silt and clay is the size distribution of mineral solid particles. The characteristic size distribution of sand, silt and clay particles is shown in following table.

Soil particle size [2]

Particle	Diameter (mm)	Number per 1 gram of soil	Surface area (cm^2) per 1 gram of soil
Sand	0.05−2	89×10^5−112	15−308
Silt	0.002−0.05	2×10^7	888
Clay	<0.002	4×10^{11}	4×10^5 (non-swelling) 8×10^6 (swelling)

A valid concept of the nature of soil must take into account not only the common perception that soil is simply a mixture of unconsolidated material resulting from the weathering processes of underlying rocks, but is a natural body, having mineral and organic component as well as physical, chemical and biological properties. Therefore, the combined properties of all soil components cannot be considered to be reflective of soil. Any classification of soil suffers from the disadvantage that it is impossible to relate it to the great complexities of soil genesis and properties. The terms used in defining the soil in different systems seldom is exactly equivalent.

Soil composition is extremely diverse and its formation is governed by many different factors like climatic conditions, parent material, relief, organisms and time, the former two being the most predominant ones. Soil is described as a three-phase system namely: Soil solid (mineral and organic), liquid and gaseous. The properties exhibited by soil are representative of the physical and chemical equilibrium of three phases. The chemical compositions of the solid component of soil, its mineral structure and the state of dispersion are the main factors influencing soil properties.

The formation of soil from parent material is a two-stage process. The first being a destructive stage -the disintegration of the primary mineral constituents of the parent rock by the physical and chemical processes of weathering. The second stage (pedogenesis), the constructive stage – resulting in the formation of a soil profile from the weathered rocked material. As a result of this interactive process a mature soil is developed as the end product. The distinction between weathering and pedogenic processes, mainly controlling the finally developed soil, cannot be made effectively on the grounds that they may occur at the same time at the same locales.

1.2 SOIL CONSTITUENTS

As a rule, soil is a three-dimensional framework, made up of a solid, a liquid and a gaseous phase, wherein proportion of each phase is a function of the quantity of its constituents and their kinetic roles in the complex series of reactions, leading to soil formation. Following figure illustrates the composition by volume of an average soil.

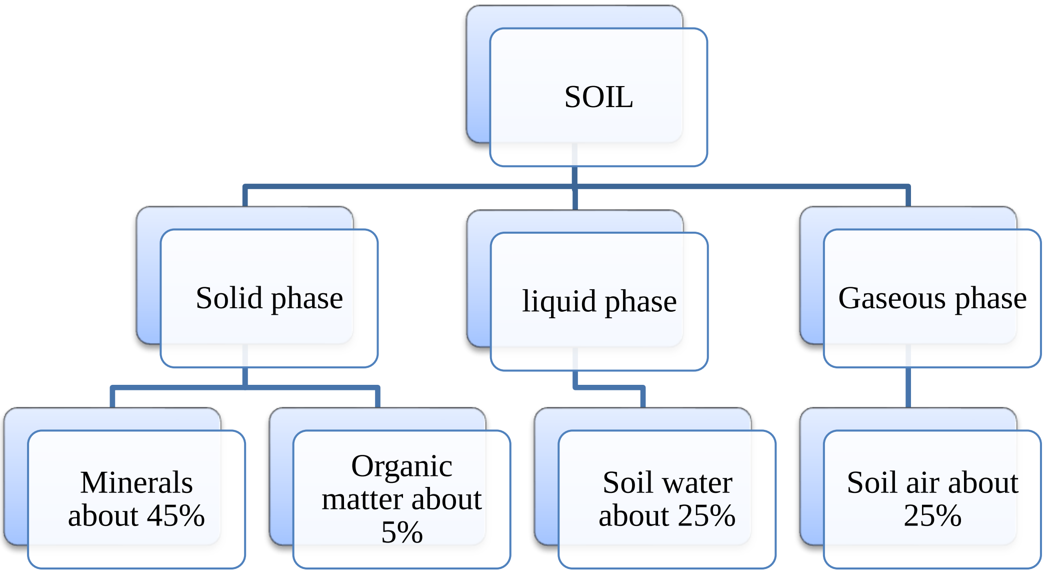

Fig. 1. Composition by volume of an average soil

THE SOLID PHASE--

MINERALS-

Weathering and pedogenic processes are steady hazard to the mineral constituent of soil inherited from the parent rocks. The processes of degradation and neo formation of minerals and their reaction with organic compounds complicates the soil mineral system, which may not be in equilibrium with the soil solution. According to the susceptibility to weathering processes, the prevailing primary minerals in soil inherited from the parent material can be arranged as

- Series of felsic minerals; plagioclase > K-feldspar muscovite > quartz,
- Series of mafic minerals; olivine>pyroxenes > amphiboles > biotic.

The importance of soil minerals is high as they have high surface area and equip the soil with ions while its dissolution. Some soil minerals may be charged and participate in exchange reactions.

ORGANIC MATTER-

The 5%weight of soil comprises organic matter mainly contributed by dead parts of vegetation and animals along with airborne dusts and applied chemicals. The presence of multitude of organic matter in soil with different particle size and different degrees of decomposition gives rise to organics with different solubilities and functional groupings.

THE LIQUID PHASE – SOIL WATER

A considerable bulk volume of soil is usually occupied by voids which may be completely or partially filled with water. Precipitation and groundwater are the chief resources for soil water. The climate and the water balance between the atmosphere and the plant-soil system are the main factors affecting the amount of soil moisture. The water loss from soil is the sum of evaporation and plant transpiration, the combined process being evapotranspiration which is an important part of water cycle and depends directly on the climatic conditions as well as the properties of the plant-soil system. The soil water retains the salts in solution and thus the soil water acts as an aqueous solution of salts.

THE GASEOUS PHASE – SOIL AIR

Soil air is the characteristic name given to gaseous phase of the soil wherein the soil pores get filled with air that is the mixtures of gases, as the water drains from soil pores. Mass flow of these gases in the aerated zone is dependent on the difference in total pressure between the soil air and the atmosphere. This pressure difference is governed by temperature, pressure, and moisture conditions. The composition of soil air is slightly different from that of atmospheric air. It contains 1–6% less oxygen, more CO_2 (10 to 150 times) and an increased amount of water vapour than atmospheric air.

The CO2 content in the soil increases due to the decomposition of organic substances by soil microorganisms, roots breathing, and insufficient aeration. Carbonic acid (H_2CO_3) is formed as a result of reaction of carbon dioxide with water, which is an important regulator of soil reaction (pH range of 5.2 to 6.5) and also acts directly during the plant nutrition by carbon. As a result of the differences in the concentration of CO_2 and O_2, between soil air and the atmosphere, partial pressure gradients are formed between the two systems along which CO_2 moves from the soil to the atmosphere, while the oxygen flow takes place in the opposite direction. Temperature gradients and replacement of atmospheric gases into the soil in sites by rainwater, irrigation and drainage are also the processes responsible for gas exchange between soil air and the atmosphere. Beside the major constituents, minor or trace amounts of other gases may occur in the soil air, originating from deep-seated sources or as products of organic or mineral reactions in the soil environment.

1.3 PROCESSES OF SOIL GENESIS

Weathering processes

Weathering is the integral part of the process of soil formation. A process of complex interaction between the lithosphere, the atmosphere and the hydrosphere, weathering characterises the means by which rocks, minerals are changed by physical and chemical processes into soil and other soil components. Dissolution, hydration, hydrolysis, oxidation, reduction and carbonation are the various chemical processes representing weathering. The destruction of parent minerals and removal of the elements from the minerals into solution and suspensions is a consequence of chemical weathering. In simplified form, the basic weathering processes can be defined as follows:

- Hydrolysis-dissociation of H2O into H+ and OH- ions which on combining with minerals produce new compounds

- Hydration-chemical combination of water molecules with minerals leading to increase in their water content
- Oxidation-incorporation of the oxygen into chemical components accelerated in the presence of soil moisture.
- Reduction-process of removal of oxygen and is the reverse of oxidations
- Dissolution-minerals are soluble in the aquatic phase and are removed by continuous action of water
- Carbonation- incorporation of CO_2 leads to transformation of compounds into carbonates.

The mineral composition of the earth surface environment determines the effectiveness of the above reactions.

Pedogenic processes

In addition to weathering, formation and decay of organic matter also leads to the formation of a particular soil profile. Several pedogenic processes namely leaching and evaporation of water, biochemical actions of living matter and bacteria also contribute to soil profile genesis. The four major heads under which soil forming processes are classified are as follows: -

- Additions: of organic material by decomposing vegetation and living organisms and new mineral material by wind and soil
- Losses: of the materials from the soil via leaching, erosion, evaporation
- Translocation: of these materials within the soil, both vertically and horizontally
- Transformation: of organic and minerals through chemical weathering and decomposition in the soil.

The above-mentioned processes are both constructive and destructive in nature. The nature of eventual soil that is formed is governed by the following six factors -

- Parent material (the nature of minerals)
- Topography (slope or landform)
- Vegetation and other soil biota
- Anthropogenic activity (degradation, fertilisation, mis -management re-cultivation)
- Climate (temperature, rainfall, wind, ice formation etc)
- Time

Thus, various interactions between the soil, solid and gaseous phases, biota and the soil solutions govern the dynamic equilibrium between soil components

1.4 TRANSPORT IN SOIL

The transport of dissolved solutes may take place through the soil solution (diffusion) via Brownian motion of ions (molecules) and also with the moving soil solution (mass flow, leaching). Solutes are also transported by mass flow, however for those solutes, which have a low concentration in the soil solution, diffusive flux, dominate the transport process.

Molecular diffusion plays an important role in the hydrodynamic dispersion of species dissolved in water flowing through soil. A solute applied as a pulse to a solution flowing through soil will disperse increasingly as it moves down. This arises from both convection and from molecular diffusion and the relative importance of each depends on the flow rate and packing characteristics of the soil.

The leaching of solutes downward to the profiles is found to be greater than their accumulation in soils of cool and humid climate, except for their higher input. In contrast to this the upward translocation of solutes dominates in the soils of warm, dry climate.

Adsorption

The term “adsorption” is commonly used for the process by which constituents from solution get attached to the surfaces of soil particles. Surface characteristics of organic and inorganic components of soils and the corresponding environmental factors govern the adsorption processes in soil. Adsorption of ionic species at charged surfaces is caused by electrostatic forces and can be explained by Coulomb’s law of attraction between unlike charges and repulsion between like charges.

Large amounts of the solute ions in the soil are bound to soil particles, particularly clay particles. This binding is possible because the clay particle surface has a net negative charge, thus causing it to attract solute ions to the surface forming a diffuse double layer (Figure .2).

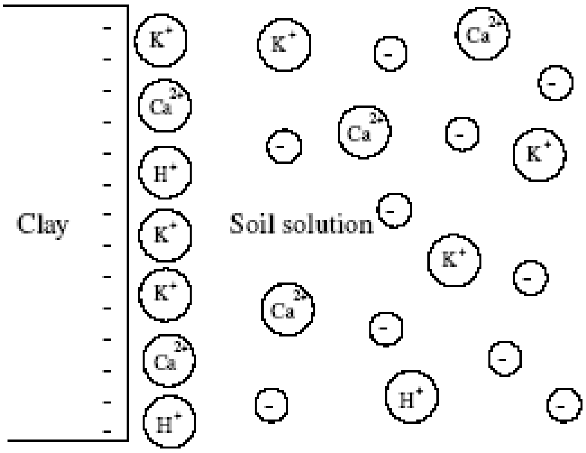

Fig. 2. Formation of diffuse double layer

The mobility of adsorbed ions is linked to their degree of hydration. It is assumed that the mobility of anions that are covalently bound to the surface is negligible with respect to liquid phase diffusion. Similarly, the adsorbed phase diffusion of un-hydrated cations may be a rate-limiting step in the weathering of minerals and the adsorption and desorption. Mobility of cations in the adsorbed phase is often ignored or introduced as an excess term

Summing up, it is concluded any solute/element introduced in to the soil may go through any of the following processes

- Occlusion or getting fixed into soil minerals,
- Incorporation into biological material,
- Dissolution in soil solution,
- Precipitation with other compounds in soils

1.5 SOIL POLLUTION

The persistence high presence of toxic chemicals, contaminants and salts, radioactive materials which have adverse effects on plant growth, wild life, humans and soil itself can be defined as soil pollution.

The presence of man-made chemicals or other alteration in the natural soil environment is the major causes of soil pollution. The reasonable use of chemical compounds like pesticides, petroleum hydrocarbons, solvents etc is beneficial for agricultural production improvements and some kind of disease controls also. But the remnants of these chemical compounds and the ability of soil to tether various chemicals makes it a major reservoir for contaminants. These chemicals are bound to soil particles under the action of different forces and exist in various forms in soil. In order to avoid health risks from these toxic chemicals it is imperative to study and understand the interaction between them and soil as the toxicity of chemicals may strongly depend on the form in which they exist in the environment. The equilibrium, found in soil environment, is a function of soil variability and some environmental properties (e.g. precipitation, climatic factors), which on alteration causes leaching of toxic elements and ions like fluoride tightly bound to soil particles.

A highly influential soil forming process, leaching is primarily responsible for migration of soil nutrients and pollutants. Leaching occurs either by active transport mostly directly by excess precipitation or passive permeation due to soil acidification. Improper application or overfertilization in agricultural areas is a potential threat to the ground water quality chiefly because of leaching of salts through macropores along with percolating water [3]. As the water moves through the soil profile, it dissolves additional salts from the soil and transports them to subsurface and ground water [4]. The relative mobility or fluidity of water along with salt movement defines the leaching rates of salts because diffusion of salt is accompanied by diffusion of water in saturated soils. This infiltration of pollutants into soil and resultant leaching during irrigation, rain events and water percolation leads to contamination of subsurface and ground water [5]. Macro porosity of soil and laminar flow of water in cracks and channels in soil may affect leaching [6, 7]. Soil type, vegetation, applied water quality, ion exchange [8], pH [9], temperature, initial moisture content [10] also affect leaching process in soil.

The fluoride wastes mostly produced by the industries dealing with aluminium, steel, glass and fertilisers find their way into the environment due to their interactive and reactive nature. In general, they may react with particular species, change oxidation states and precipitate [11] or may be bound or sorbed by particular natural substances, which may change their mobility. The study of distribution of an element amongst defined chemical species is called speciation [12].

Sorption of Fluoride in Soil

Sorption in soil is a physicochemical process wherein one substance gets attached to another either by absorption or adsorption and thus immobilises the introduced foreign substance like fluoride ions. The principal factors governing the sorption in soil are sorprtive concentration i.e. amount of clay and organic fraction, solution pH, sorptive size, water content, temperature of the soil and sorptive and sorbent charge [13].

The soil sorption complex comprises of clay minerals, oxides, sesquioxides and hydrous oxides of minerals. The total amount of clay minerals in soil bulk is a deterministic factor in the soil sorption complex.

In case of high fluoride surface loading conditions increasing pH reduces fluoride adsorption. Also, in presence of competing anions fluoride adsorption reduces.

Solute Transport Processes

The study of solute transport processes in soils is important as some chemicals are required for soil and plant health (e.g. micronutrients) and other chemicals may be highly toxic particularly if they are present in high concentrations. The study of the fate of contaminants is vital to control the extent of contaminant migration in the subsurface. These processes can be classified on the basis of type of contaminant. For dissolved (non-reactive) contaminants, uninfluenced by chemical reactions or biodegradation, the three main processes of transport in soil subsurface are: advection, diffusion and dispersion. In case of reactive solutes, the transport is also governed by adsorption/desorption, chemical reactions, dissolution, precipitation and biodegradation along with the above-mentioned processes.

1.6 MATHEMATICAL APPROACH TO FLUORIDE TRANSPORT

The development of industry and agriculture has resulted in increase in the amount of contaminant entering the subsurface system and polluting soil and groundwater and resultantly affecting human health. Fluoride is a naturally present contaminant and finds its way in the soil environment via agricultural operations like application of pesticides containing phosphates or release of industrial wastes. Mathematical models are pivotal to understand the migration and mobility of a contaminant/fluoride ion in soil and predict their fate.

The fundamental solute transport equation also known as the advection-dispersion equation along with the case specific initial and boundary conditions forms solute transport model. The following points define the classical definitions of advection, diffusion and dispersion and then delves in to the solute transport equation.

Diffusion

Diffusion, a micro-scale process is caused by the random movement of molecules of solute dissolved in water. It results in migration of contaminant from the area of a higher concentration to the area of a lower concentration. Thus, diffusion ceases to occur when the difference in concentration i.e. the concentration gradient becomes zero. Diffusion is independent of fluid flow and also the direction of contaminant movement. Diffusive transport is described using Fick’s first law of Diffusion.

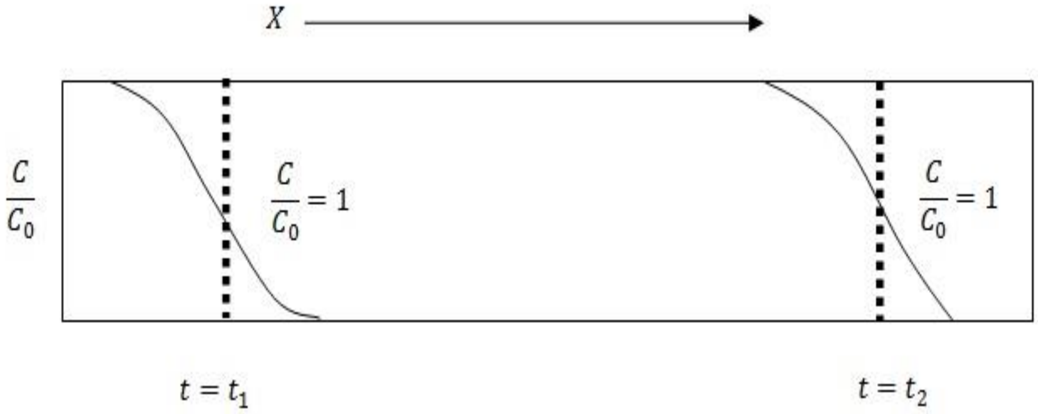

Fig. 3. Diffusion only

Advection

Advection refers to the transport of dissolved contaminant with (in) the moving fluid i.e. groundwater., and it refers to the average linear flow velocity of the bulk of contaminant. Due to advection the average velocity of contaminants is assumed to be same as that of average fluid velocity.

The seepage velocity can be represented as

$$v_s = \frac{K_c h}{\alpha} \tag{1}$$

Where, K_c is the hydraulic conductivity, h is the hydraulic gradient and α is the porosity of the porous material.

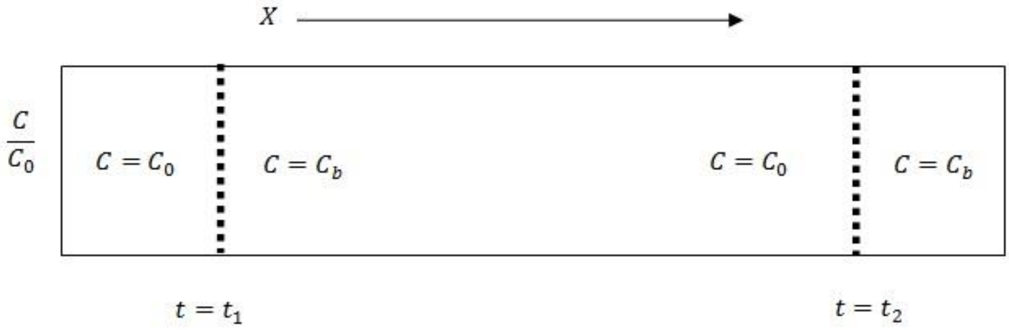

Fig . 4. Advection only (Where C_0 =Initial Concentration, C_b =Background Concentration)

Dispersion

The spreading of dissolved contaminants as a result of heterogeneous distribution of groundwater velocities within and between different soil pores is defined as dispersion. The contaminant flux is dependent on its charge, pore size, path length and friction in pores. Mechanical dispersion takes place on the pore scale and is caused as a result of variable velocities across the pore cross section.

This summed up effect of mechanical dispersion and molecular diffusion is called hydrodynamic dispersion. Mechanical dispersion dominates molecular diffusion in the liquid phase, except when the fluid velocity is relatively small or is negligible whereas diffusion dominates the subsurface transports in low permeability media e.g. clays, rock matrices etc. Longitudinal dispersion takes place along the direction of the flow path and transverse dispersion along direction normal to the direction of the flow path. Figure .5 represents the one-dimensional dispersion of the contaminant results in a dilution of the contaminants at the advancing edge of flow by considering only longitudinal hydrodynamic dispersion [16,17].

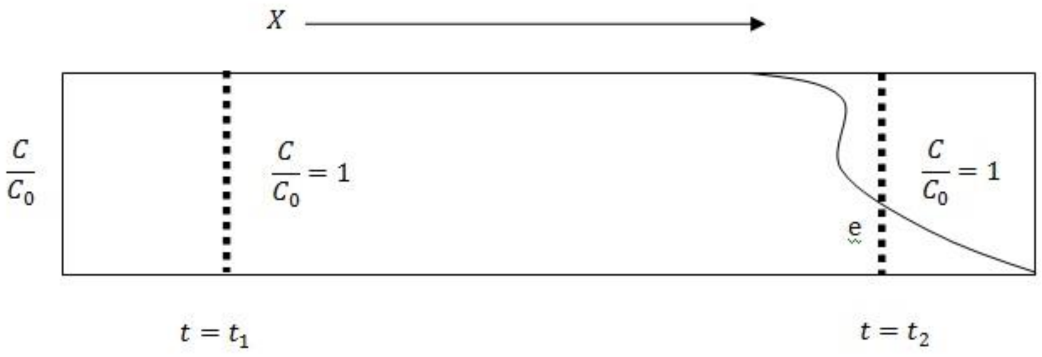

Fig. 5. Advection and Dispersion

Hydrodynamic Dispersion Equation

The fundamental equation governing transport of dissolved contaminants the advection-dispersion equation which is obtained by combining the contaminant mass balance with Fick’s first law of diffusion.

Fick’s first law of Diffusion

Fick's first law of diffusion describes the movement one specie through the mixture of specie and fluid as a result of concentration gradient of specie. It states that the rate of diffusion of a solute substance through the unit area of a section is proportional to the concentration gradient of the solute normal to that section.

$$J_D = -D\frac{\partial c}{\partial x} \tag{2}$$

where, J_D is the diffusive mass flux, D' is the diffusion coefficient. Negative sign indicates that contaminant moves from zone of higher concentration to the zone of lower concentration.

Advection-dispersion Equation

Let the concentration of the fluid at any point (x, y, z) be $c\ (x, y, z)$ and q_x, q_y, q_z are the velocity components parallel to the co-ordinate's axes. Consider a small element of volume $dxdydz$ in the form of a rectangular parallelepiped shown in Figure. 6 whose sides are parallel to the axes of co-ordinates.

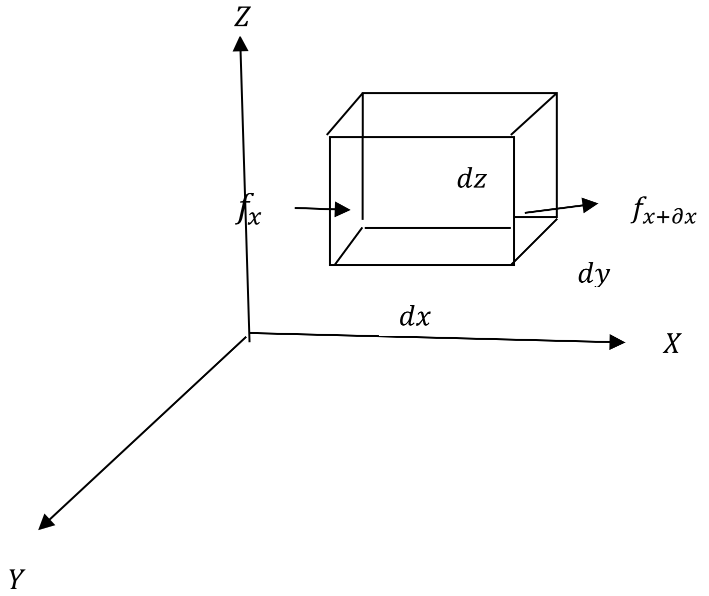

Fig .6. Small rectangular parallelepiped

Let J_D (J_x, Jy, J_z) represent the dispersive mass flux. Then by Fick's first law of diffusion

$$J_x = -D_x \frac{\partial c}{\partial x}, J_y = -D_y \frac{\partial c}{\partial y}, J_z = -D_z \frac{\partial c}{\partial z}, \tag{3}$$

where D_x, D_y, and D_z are the dispersion coefficients.

Let the convective mass flux be J_c through the element can be written as,

$$J_c = qc. \tag{4}$$

$q\ (q_x, q_y, q_z)$ is the flow velocity.

Therefore, the total flux combining the advective and diffusive transport is

$$\bar{J}(J_1, J_2, J_3) = J_c + J_D \tag{5}$$

The total flux entering the element along x-direction

$$J_1 = \left(q_x c - D_x \frac{\partial c}{\partial x}\right) \partial y \partial z = f_1(x, y, z) \tag{6}$$

And the total flux leaving the element from x-direction

$$f_1(x + \delta x, y, z) = f_1(x, y, z) + \frac{\partial f_1(x, y, z)}{\partial x} \partial x + \cdots \tag{7}$$

The net solute influx along x-axis can be written as

Difference of mass per unit time = mass entering the element – mass leaving the element

$$= -\frac{\partial f_1(x,y,z)}{\partial x} \partial x$$

$$= -\frac{\partial}{\partial x}\left(q_x c - D_x \frac{\partial c}{\partial x}\right) \partial x \partial y \partial z \tag{8}$$

(using Eq. (6))

Similarly, the excess of solute flow along y-axis

$$= -\frac{\partial}{\partial y}\left(q_y c - D_y \frac{\partial c}{\partial y}\right) \partial x \partial y \partial z \tag{9}$$

And the excess of solute flow along z-axis

$$= -\frac{\partial}{\partial z}\left(q_z c - D_z \frac{\partial c}{\partial z}\right) \partial x \partial y \partial z \tag{10}$$

So net solute influx from all the co-ordinates axes of the element, i.e. difference of mass of solute per unit time

$$\begin{aligned} = -\Bigg[&\frac{\partial}{\partial x}\left(q_x c - D_x \frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(q_y c - D_y \frac{\partial c}{\partial y}\right) \\ &+ \frac{\partial}{\partial z}\left(q_z c - D_z \frac{\partial c}{\partial z}\right) \partial x \partial y \partial z\Bigg] \end{aligned} \tag{11}$$

Assuming the dissolved substance to be non-reactive, the difference between the flux into the element and the flux out of the element equals the amount of dissolved substance accumulated in the element. Therefore, the rate of mass change per unit time is given by

$$= \frac{\partial c}{\partial t} \partial x \partial y \partial z \tag{12}$$

By the law of conservation of mass,

Rate of change of solute concentration = Rate of solute flow in - Rate of solute flow out

$$\frac{\partial c}{\partial t}\partial x\partial y\partial z = -\left[\frac{\partial}{\partial x}\left(q_x c - D_x\frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(q_y c - D_y\frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(q_z c - D_z\frac{\partial c}{\partial z}\right)\partial x\partial y\partial z\right] \tag{13}$$

$$\frac{\partial c}{\partial t} = -\left[\frac{\partial}{\partial x}\left(q_x c - D_x\frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(q_y c - D_y\frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(q_z c - D_z\frac{\partial c}{\partial z}\right)\right] \tag{14}$$

Above is the hydrodynamic dispersion equation or advection-dispersion equation for three-dimensional system.

Here, D_x, D_y and D_z are the dispersion coefficients, which may be function of time or position or constant.

For one-dimensional case, the advection-dispersion equation with constant coefficient reduces to

$$\frac{\partial c}{\partial t} = D_x\frac{\partial^2 c}{\partial x^2} - q_x\frac{\partial c}{\partial x} \tag{15}$$

Initial and Boundary Conditions

The advection-dispersion equation needs to solved in conformation with the information related to specific case of flow which are classified as initial and boundary conditions of the case under study.

Initial Condition

The initial conditions as the name suggests states the value of the variable under consideration at some initial time $t=0$ (usually). For a three-dimensional system the initial condition for concentration of solute transport is given as

$$c(x, y, z, t) = c_i(x, y, z, 0) \tag{16}$$

Where $c\ (x, y, z, t)$ represents the concentration at any value of the variables involved and $c_i\ (x, y, z,0)$ is a known function or constant or zero as per the physical model of the problem. Initial conditions are required for time dependent problems and give the information about the time before contamination.

Boundary Conditions

The solute transport problem must also consider different interactions between the transport domain and its environment as magnitude of water fluxes across the domain boundaries is determined by them. These interactions represented mathematically constitute the boundary conditions for the problem under consideration. The boundary conditions usually employed for a solute transport problem are classified into three types as follows

A. **Neumann boundary condition:**

This boundary conditions are employed when the total mass of a solute across a boundary is defined. It is often used to inflow boundaries like experiments and also in field locations which are dealing with point source of pollution and the total solute mass entering the groundwater is known or can be estimated [18]. As the total mass leaving the system is not known this type of condition cannot be defined for outflow boundaries. Mathematically this is represented as

$$\left(D_{ij}\frac{\partial c}{\partial x_j}\right)n_j = f(x,y,z,t) \tag{17}$$

where, *f (x, y, z, t)* is a known function and n_i is direction cosine. For impermeable boundaries, *f (x, y, z, t)* becomes zero.

B. **Cauchy boundary condition:**

The mass flux of solute across the boundary is dependent on the concentration in water phase. Cauchy boundary condition is applied at the outflow boundary. Mathematically, it is expressed as

$$\left(D_{ij}\frac{\partial c}{\partial x_j} - q_i c\right)n_i = f(x,y,z,t) \tag{18}$$

where, $f(x,y,z,t)$ is a known function. The first term on the left-hand side represent flux by dispersion and the second term represent the effect of advection. These descriptions of boundary conditions have been explored [19].

C. **Dirichlet boundary condition**:

This condition refers to the case when the concentration at the boundary is known or fixed, though practically it is almost always impossible. It prescribes concentration along a portion of the boundary. It is given in the following form

$$c(x, y, z, t) = c_0(x, y, z, t) \quad (19)$$

Where, $c_0\ (x, y, z, t)$ may be a function of space or time or both or a constant.

1.7 SOLUTION OF THE MODEL

Analytical Method

The traditional way of solving the advection-diffusion equations are the analytical methods. These methods provide solutions which are useful in investigating the effects of different parameters and also extrapolate the result over large time and spatial values. The literature is replete with many analytical solutions for advection-diffusion equation [20, 21].

The various methods which can be employed to find the analytical solution of advection-diffusion model are namely-Transform calculus involving Laplace transform technique, Fourier transform technique, generalized integral transform technique, Hankel transform technique, Green's function method, Power series method, Method of superposition principle, Variational methods and similarity transformations. The solution obtained as such, is only true for certain initial and boundary conditions and in certain cases it includes special functions like Bessel and error functions whose convergence is difficult to compute [22].

Numerical Solution

Numerical methods are also employed to approximate the solution of the solute transport model. They have larger flexibility with regard to the modifications in initial, boundary and physical conditions. With the increase in the dimension of the problems numerical methods find more applicability. The solution so obtained may be generalized to the cases of different zones without any simplification of assumptions. The various methods may be broadly classified into three groups:

i. Eulerian
ii. Lagrangian
iii. Mixed Lagrangian-Eulerian methods

Both Eulerian and lagrangian approach make use of finite difference or finite element method to discretize the transport equation. The former method uses a grid system whereas in the later the mesh moves along with the flow or remains fixed in a deforming coordinate system. In Lagrangian-Eulerian approach, a two-step procedure is followed. Using a Lagrangian approach, first convective transport is considered in which Lagrangian concentrations are estimated from particle trajectories. Later the Eulerian approach is undertaken to model all other processes including sinks and sources. With the help of any finite element or finite differences method, the final concentrations are estimated. These methods are still many of the popular methods being used today also. It has been observed that these methods give good results for dispersion dominant transport processes. In case of convection dominated transport processes both methods can lead to significant numerical oscillations and/or artificial dispersion problems. However, such deviations can be eliminated by selecting an appropriate combination of relatively small space and time steps.

Finite Difference Method

Finite-difference methods [23,24,25] and Finite difference equations are used in this numerical method to approximate the solutions to differential equations. The solutions to differential equations are approximated by replacing derivative expressions with approximate equivalent difference quotients. As the first derivative of a function f is, by definition,

$$f'(a) = \lim_{h \to 0} \frac{f(a+h) - f(a)}{h}$$

then a reasonable approximation for that derivative would be to take

$$f'(a) \cong \frac{f(a+h) - f(a)}{h}$$

for some small value of h. In fact, this is the forward difference equation for the first derivative. Similarly, backward difference and central difference formulae are also used to replace derivative expressions in differential equations and approximate their solutions using Implicit or Explicit finite difference method or Crank Nicholson method.

Finite Element Methods

The finite element method (FEM) [26] is a numerical method to find approximate solutions of partial differential equations partial differential (PDE) as well as of integral equations. The procedure involves either elimination of the differential equation completely (steady state problems), or transforming the PDE into an approximating system of ODE, which are then numerically integrated using standard techniques such as Euler's method, Runge-Kutta method, etc.

The Finite Element Method is a good choice for solving partial differential equations over complicated domains, changing domains, when the desired precision varies over the entire domain, or when the solution lacks smoothness.

Galerkin methods:

In Galerkin methods [27, 28] a continuous operator problem e.g. a differential equation is solved by first converting it to a discrete problem. Principally, it is the conversion of the equation to a weak formulation by applying the method of variation to a function space. Some constraints are then added on the function space in order to characterize the space with a finite set of basis functions.

Finite Volume Methods

In this method [29,30] partial differential equations are expressed and solved by transforming into algebraic equations. Though structured mesh is not required but may be used and values are calculated at discrete places on a meshed geometry. "Finite volume" refers to the small volume surrounding each node point on a mesh. Using the Gauss’s divergence theorem volume integrals in a partial differential equation containing a divergence term are converted to surface integral, which are then evaluated as fluxes at the surfaces of each finite volume. These methods are conservative on account of the conservation of fluxes entering and leaving a given volume.

1.8 AIM AND OBJECTIVE

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 [31]. It has been established that prolonged intake of high amount of Fluoride by human body may cause permanent bone deformation [32]. Plants being an important constituent for the dietary intake of Fluoride, the Fluoride sorption by soil has been a topic of investigation by many researchers [33,34].

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 [35]. The adsorption and leaching processes directly affect fluoride migration and exchange from soil to water. In soil, some of the fluorides get immobilized due to adsorption and some part of it gets percolated in the ground.

The study of fluoride transport will be helpful in understanding the behaviour of fluoride ion under different pH, ionic strength and the presence of competing ions. It will also be of great help in designing and operating fluoride removal methods as per local water qualities and also how the groundwater contamination can be avoided.

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. They may be used to determine the quantity and transport of fluoride that may occur, under the influence of soil environment (pH, presence of other ions like Al, Na, Ca, Mg) to develop the action plan for the necessary and immediate remedial action, and to stop potential exposure concentrations at receptor points.

For protection of public health and the environment, especially to stop the deterioration of the groundwater quality, it is desirable to retard the dissolution and transport of the pollutant ions to water.

1.9 IMPORTANCE OF PROPOSED RESEARCH WORK

The present research work aims to quantify the total concentration of fluoride ion in the soil, which will help in estimating the pollution profile of the soil and groundwater. Fluoride is a pervasive micro pollutant in groundwater and one of the major chemicals causing large scale health problems like fluorosis through exposure to drinking water. Globally more than 70 million people are estimated to be suffering from fluorosis [36].

This research work is important in understanding the transport phenomena of Fluoride ions in different soil environment. A quantitative description of Fluoride ion transport in the saturated and unsaturated zone of the soil will be helpful to predict the impact of soil type, physicochemical properties etc. on the groundwater contamination.

In this work, Fluoride ion transport in soil under varying lithospheric conditions (pH, conductivity, Calcium and magnesium levels, soil alkalinity, fertilizer applicability etc.) will be studied by using mathematical modeling. Each model will be preceded by the underlying physical concept, and will then be translated into a mathematical model.

The modeling concepts will be coupled with an overall mathematical framework so as to be practically useful for environmental problems. The work will be primarily devoted to various issues related to the modeling dynamics of Fluoride ion in soil and soil environment. With respect to the mathematical approach, the work will explore application of fundamental mathematical principles for understanding and quantifying the fluoride pollution. Special emphasis will also be given to the characterization of spatial variability and the influence of effective parameters which will make the research more applied.

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Chapter 2

Review of Literature

The dangers of soil pollution are increasing with each passing day as contaminants added into soil as pollutants are either percolated into subsurface and ground water through infiltration or leaching. Modern agriculture practices make use of numerous pesticides, fungicides, bactericides, insecticides, biocides, fertilizers and manure resulting in severe biological and chemical contaminants of agriculture lands. Crops grown on such lands are reported to contain high level of pollutants [1, 2], consequently pose threat to human health by entering the food chain.

Fluoride is one of the contaminants which has attracted worldwide attention. It is necessary element for human and animal health and occurs naturally in soils and rocks as calcium fluoride, cryolite, and fluorapatite. At a certain low concentration in drinking water it is essential for the human body in preventing dental decay and strengthening skeletal system [3]. However, if the amount of fluoride pollutants getting drained into the soil is more than a certain level and exceeds the capacity of self-purification of the soil, fluoride will further leach downwards with water and pollute groundwater. This presence of fluoride in the groundwater and crops and resultant consumption by human being may cause bone diseases, blotchy teeth and ulcers of thyroid, liver and other organs [4].

According to Zhang and Su Bao [5], the fluoride ions are chemically reactive and migration processes in soil are complex. As a result of adsorption and desorption, the value of concentration peak in its breakthrough curve gets gradually decayed. As a result of conversion and immobilisation of fluoride ions due to presence of other elements in the soil OH ions are released and pH of the soil increases. Ultimately, leaching of fluoride ion is also responsible for increase in alkalinity of soil. Consequently, subterranean water sources are also jeopardized because of rapid leaching.

2.1 FLUORIDE POLLUTED SOILS

The World Health Organization (WHO) guideline value for maximum contaminant level (MCL) for fluoride in drinking water is 1.5mg/L [6] whereas the same is 4mg/L [7] as established by the US EPA. However much greater levels of fluoride in water have been measured in regions across many countries.

The fluoride concentration in southern Lakeland, California is approximately 5 mg/L [8]. As high as 20 mg/L fluoride concentration in groundwater is measured in some regions of North Africa [9]. The belt that stretches from Syria through Jordan, Egypt, Libya, Algeria, Sudan and Kenya, and from Turkey through Iraq, Iran, Afghanistan, India, northern Thailand and China have recorded high-fluoride levels.

In India high fluoride concentration in ground water (>1 mg/l) has been found to be widespread in the arid to semiarid western states of Rajasthan and Gujarat and in the southern states of Andhra Pradesh, Karnataka and Tamilnadu [10]. India lies within the geographical fluoride belt which extends from Turkey to China and approximately 12 million of the 85 million tons of fluoride deposited on earth’s crust was found in India [11] Excessive fluoride in drinking water caused dental fluorosis, skeletal fluorosis and general health problems. About 20 states of India have been identified as endemic for fluorosis with highest presence being reported from Andhra Pradesh, Haryana, Karnataka, Punjab, and Tamilnadu.

2.2 BRIEF OVERVIEW OF FLUORIDE

Fluoride, an ionic form of fluorine, is widely distributed in atmosphere. In low concentrations it is an important element for human and animal health. However, if the concentration exceeds a permissible value it tends to assimilate in sediments and pose a high threat to the atmosphere mainly when it meets conditions that enhance its solubility and concentration in soils, water, sediments and organisms. Thus, it acts as a persistent and non-degradable toxin that gets accumulated in soils, plants, wildlife and humans [12].

2.3 FLUORIDE CONTAIMINATION SOURCES

The sources of fluoride contamination of soil can be classified into two main types namely - natural and anthropogenic sources. Anthropogenic activities perpetuate the pollution of environment as compared to the natural sources.

Natural sources-

Naturally, Fluoride is found in soils and rocks as calcium fluoride, cryolite, and fluorapatite. The natural weathering of fluoride bearing rocks due to hydration and hydrolysis reactions; loss of mineral components via leaching and volatilization; dissolution and dissociation of minerals; oxidation and reduction reaction; immobilization by precipitation; and chemical exchange processes such as cation exchange cause discharge of fluoride into the soil. However, the concentration of fluoride poses a threat only when it increases above the permissible value in the environment. The contamination may be a point source contamination or diffused one by carrying out of fluoride to different places by surface erosion or runoffs.

Anthropogenic sources-

The advancement in the fields of agriculture and industry has been accompanied by increase in anthropogenic activities, which are the major causes for the observed elevation of fluoride concentration worldwide. Anthropogenic activities such as use of phosphate fertilizers, pesticides, sewage and sludge for agriculture, airborne emissions from aluminium smelters, phosphate processing plants, enamel factories, depletion of groundwater, etc., are also responsible for increased fluoride concentration in soil. The fate of such fluoride dissolved in soil may vary from being immobilized by the soil [13] or up taken by plants and cause toxicity in them as well as microorganisms [14]. It also finds its way into surface water and water body of shallow groundwater through leaching and causes high fluorine contamination of groundwater [15].

The significant increase in anthropogenic discharge of fluoride in the atmosphere and its resultant effect on human and animal health has given rise to universal concern for the implementation of methods that would decrease their release in the environment and also develop treatment methods for defluorination.

2.4 FACTORS AFFECTING FLUORIDE AVAILABILTY IN SOIL

The chemical properties of fluorine are active and there are many factors which affect its migration and accumulation in soils. It may get subdivided into adsorbed, precipitated, and water-soluble phases which cannot be completely dissociated from each other. Fluorine in soil is in dynamic equilibrium with the two geochemical processes namely enrichment and leaching which mirror its adsorption and desorption by clay minerals respectively. [16].

The principal parameters governing these two processes are the geochemical properties of soil and clay minerals, soil’s sorption capacity which is a function of the soil pH, types of sorbents present and soil salinity. Presence of anions and competing toxic elements also affect fluoride adsorption.

The mobility and solubility of contaminants in the environment is markedly affected by their surface chemistry. Thus, the reactions between solutions and solids often involve the interface between these phases. The dissociation of water molecules as a result of its interaction with the contaminant releases OH^- ions which occupy the surfaces of contaminants and soils in water.

Effect of pH –

The pH is the most important factor that controls adsorption of fluoride to soil. It has been reported to be maximum at pH 5.5 [17]. Most of the Fluoride gets complexed with either aluminium or iron in soils with pH below 6 [18,19]. If sufficient calcium carbonate is present in soil with pH greater than 6.5, fluoride gets completely fixed in soil as calcium fluoride [20]. As the concentration of protonated surface sites acting as fluoride binding sites decreases significantly with increase in pH, fluoride adsorption shows a tremendous drop. This was observed at pH 8.8 for adsorption at activated alumina sites [21]. As a result, the possibility of migration of soluble fluoride to the groundwater is most prominent at all temperature in alkaline environment i.e. pH .7.0[22].

Fluoride has different species in water, including HF, HF2−, and F−. The deprotonation reactions of HF and HF2− are written as [23]

$$HF \leftrightarrow H^+ + F^-; pK_{a_1} = 3.18\,;\ [HF] = \frac{[H^+][F^-]}{K_{a_1}}$$

$$HF_2^- \leftrightarrow H^+ + 2F^-; pK_{a_2} = 3.76\,;\ [HF_2^-] = \frac{[H^+][F^-]^2}{K_{a_2}}$$

Because the total dissolved fluoride is

$$F_D = [HF] + 2[HF_2^-] + [F^-]$$

The fluoride ion concentration is expressed as

$$[F^-] = \frac{\sqrt{\left\{K_{a_2}([H^+] + K_{a_1}\right\}^2 + 8K_{a_1}{}^2K_{a_2}[H^+]F_D - K_{a_2}[H^+] + K_{a_1}}}{4K_{a_1}[H^+]}$$

Effect of OH Ions-

As the radii of F- and OH- ions are almost of the same dimension, an exchange of OH- and F- is inevitable which showed increased fluoride leaching with increase in OH- concentrations. Unlike other soluble ions, F-is not leached much from naturally salinized salt affected soil rather it is redistributed within the soil profile. The adsorption of F- to soil increases with decrease in soil pH in acidic soil while in most of the alkaline soil F- is replaced by OH- ion producing high leachable concentration of ionic fluoride [22, 24]. Thus, the leaching rate of F- is always found higher in an alkaline soil.

Effect of Cations-

Fluoride leaching is significantly affected by the cation attached to the OH- ions. It has been observed to follow the following order $NH_4OH > NaOH > KOH$ the maximum being with NH_4OH and minimum with KOH [22].

NH_4^+ ions can bind at least 4 F^- ions through H-F bond [25]. As a result the concentrations of leachable fluoride $[F^-]_i$ and rate of leaching (LRobs) were found to be highest in the experiment by Saxena et al[[22].As the lattice energy of KOH is more than that of NaOH the availability of free OH- ion is more in NaOH relative to KOH Thus the replacement of OH- ions is more in presence of NaOH as compared to that of KOH. Some earlier studies on adsorption and desorption of F- on soil of China interpreted as competing sorption of OH- in soil solution replacing some F- from surface of soil colloids resulting in increase in leaching of F-. The leaching rate of F- was found higher in alkaline soil than acidic. Also, the adsorption of F in soils decreased from humid areas to arid areas and from acidic soils to alkaline soils.

2.5 INTERNATIONAL AND NATIONAL STATUS OF WORK DONE

Various inorganic and organic contaminants degrading soil pose not only an ecological risk but at the same time also give rise to socio-economic issues as such soils become poor in physicochemical properties, susceptible to erosion, less productive and sustainable and diminished food chain quality.

A major environmental problem is non-point source pollution of groundwater by various agricultural by-products as gradual decrease of water quality may impair, in the long term, its use as potable drinking water. The control or management of this kind of pollution is difficult because of the diffusive and progressive nature of pesticide accumulation. In most cases, by the time evidence of pollution or benefits resulting from pest control become perceptible several years pass by. The assessment, cleanup and management of critical groundwater resources have been the focus of attention of civil engineers, hydro-geologists and soil scientists for several years. Similarly, the solute transport processes which controls the fate of chemicals in the near surface has been reviewed by many authors [26,27]. The key processes include sorption, degradation, volatilization and leaching.

Mathematical models may offer a solution to hydrological problems. The term "model" has been given many meanings in the hydrological literature. The simplified representation of a complex system is called a model; hydrological models (that is, models of hydrological systems) being either: (a) physical, such as a scaled-down facsimile of the full-scale prototype [28,29] (b) analog, such as the resistance-capacitance analog of a coastal aquifer used by [30] and of a complete catchment have been used [31].

Several factors may cause non-ideal solute transport, including non-homogeneous soil physical properties (e.g., hydraulic conductivity, soil-water content, bulk density), physical non-equilibrium, non-homogeneous soil chemical properties (e.g., sorption equilibrium constant), sorption non-equilibrium, sorption isotherm non-linearity and sorption-desorption non-singularity. Factors related to the physical nature of the porous medium, such as structure (i.e., non-homogeneous soil physical properties and physical non-equilibrium), will obviously control non-ideality for the transport of non-sorbing solutes and of water. It has been suggested that the primary factors causing non-ideal transport for various chemical solutes are nonhomogenous soil properties (both physical and chemical) and non-equilibrium (both transport and sorption) [32, 33].

The explanation that the observed non-ideal behaviour (e.g., "preferential flow", "macro pore flow", "channelling", "short-circuiting", "bypassing", "partial displacement", "subsurface storm flow") is the result of non-unimodal pore-size distributions (i.e., a non-uniform velocity field) is generally accepted. To model such systems, a bicontinuum approach [32] is often employed. With this approach the porous medium is considered to be comprised of two domains: a "mobile" domain, where solute transport occurs by advection and dispersion, and an "immobile" domain, in which there is minimal advective flow. The mobile-immobile conceptualization for soils dates back at least 30 years, when it was used [34]. Early mathematical models employing this conceptualization were presented [35,36]. Rapid transport in the mobile domain is accompanied by diffusive mass transfer of solutes between the mobile and immobile domains, which results in the latter behaving as sink/source components. Solute transport, as described by breakthrough curves (BTC's), in such systems is characterized by early initial breakthrough and by "tailing" or delayed approach to relative concentration values of either 0 or 1. As access to some portion of the porous medium is constrained by diffusive mass transfer, the solute in the system may be considered to be in a state of non-equilibrium, as access to some portion of the porous medium is constrained by diffusive mass transfer. This phenomenon is termed physical or transport non-equilibrium (TNE). It has been suggested [37] that "dead water" could cause non-ideal BTC's. Behaviour attributable to TNE has been observed in aggregated, heterogeneous (with respect to hydraulic conductivity) and fractured porous media as well as in macroporous media. Some of the earliest work on solute transport in aggregated soils, where the non-ideality observed in experimentally-derived BTC's was attributed to TNE, was performed [38] for non-sorbing solutes ($C1^{-}$) and for sorbing inorganic solutes (Mg^{2+}), and has been discussed by many authors [39,40,41 and 42] for organic compounds (pesticides atrazine, lindane, fluometuron and picloram). All these experiments were performed with packed soil columns and, while demonstrating the influence of soil aggregation on solute transport, they are not particularly representative of field conditions. In an attempt to more closely simulate field conditions, miscible displacement studies have also been performed using undisturbed soil cores.

Several mechanisms are involved in the solute-transfer process for a system representative of the mobile-immobile concept: (1) advective-dispersive transport from bulk solution to the boundary layer (i.e., adsorbed water surrounding the sorbent); (2) diffusive transport across the adsorbed water (i.e., film diffusion); and (3) pore and/or surface diffusion within the immobile region (i.e., intra-aggregate diffusion). Any or all of these three components may be a rate-limiting step. To simplify, it is usually assumed that one of the three steps is slow relative to the other two and that it may therefore be designated as the primary rate-limiting step. The advective-flow domain is generally assumed to be well-mixed, thus minimizing the importance of mass-transfer resistances within these regions.

Dynamic simulation models for these and other solute transport processes are timely tools for engineering/management decisions. To develop mathematical models which can be used to predict the mobility and persistence of chemicals in the unsaturated zone near surface enormous efforts have been made over the last three decades. The advances in high-speed digital computers have provided a stimulus to this age of model development but to some extent restrained by the staggering data requirements of some of the more complex models.

The importance of fluorine as a trace element , the effect of its deficiency or excess on distortion, supersession abnormality in organisms has been stated and studied [15] . Leaching dissolution of high fluorine rock and soil mass, fluoride-base aerial precipitating dust and fluoric waste water drainage from

Industrial and mining enterprises made fluorine go into surface water and water body of shallow ground water to cause high fluorine contamination.

The Fluoride uptake by plants is usually linearly correlated with total F-activity in solution [43] as has been shown by solution culture experiments. It was shown that F, as HF, was taken up more readily than F- and Al-F species [43]. The various factors governing Fluoride dynamics in soil are soil water content, soil texture, temperature and the pH of the soil. The F concentration in soil-cultivated plants was better explained [44] by soluble F in the soil together with the pH than by soluble F alone.

High concentration of Fluorides is dangerous for living beings, including humans [45, 46]. Higher content of fluorine-ions leads to the inhibition of some enzyme reactions, to the linking of biogenous elements (P, Ca, Mg etc.) and the disturbance of their balance in the organism. Many scientists have documented toxic effects of accumulation of large amounts of Fluorine in plants as well as groundwater.

The study of geochemical characteristics and the spatial distribution of the fluoride in the soils of Indo-Gangetic plains has been studied [47]. The fluoride distribution in soil profiles and surface soil (0-15 cm) samples was studied. It was concluded that the natural weathering of fluoride bearing rock and minerals various ion-exchange and distribution processes in the soil, alkalinity, sodium absorption ratio, calcium, magnesium and clay contents of the soil were responsible for high fluoride occurrence in the area.

The modification in soil characteristics related to soil biological properties indicating alteration in soil biochemical and microbiological properties can be used to assess the intensity of soil contamination. The effect of fluoride, a common problem in the semi-arid region, on seed germination, early growth and antioxidant enzyme activities of fast growing and drought resistant tree of this region i.e., Prosopis juliflor was studied [48]. The results of this study showed that root and shoot growth, vigor index decreased but catalase and peroxidise increased with substantial increment of sodium fluoride concentration. Larger portion of the fluoride was observed to be accumulated in plant roots followed by the shoot. But no morphological changes were observed in the species. Authors concluded the Prosopis juliflora is a suitable bioindicator and it could beneficently remove fluoride in phytoremediation purposes.

Fluoride contamination is also known to influence the diversity, number and behaviour of soil microorganisms. The inhibitory effect of fluoride towards the main microbial populations responsible for the removal of organic constituents and nutrients in waste water treatment processes have been evaluated by [49]. It was concluded from the results of short-term batch bio-assays that the toxicity of sodium fluoride varied widely depending on the microbial population. Nitrifying bacteria appeared to adapt rapidly to fluoride. All other microbial populations evaluated in this study i.e., glucose fermenters, aerobic glucose degrading heterotrophs, denitrifying bacteria and H2-utilizing methanogens tolerated fluoride at very high concentration (>500 mg/L).

One-dimensional transport of non-volatile solute in steady state in a homogeneous porous media with uniform soil moisture distribution is known as linear equilibrium sorption model. The dimensionless form of convection-diffusion equation considering degradation of both the phases of solute (dissolved and adsorbed) and linear equilibrium sorption isotherms is given as

$$R\frac{\partial C}{\partial t}-\frac{1}{P_e}\frac{\partial^2 C}{\partial z^2}+\frac{\partial C}{\partial z}+\mu C=0, \tag{1}$$

Where R is the retardation factor, C is the relative resident solute concentration in soil, t is the dimensionless time, z is the dimensionless space, P_e is the Peclet number and μ is the dimensionless first order degradation coefficient including both the phases. The numerical scheme representing equation (1) for a pulse type solute concentration [50]is given as

$$
\begin{aligned}
&R\frac{\partial C}{\partial t}+\mathcal{L}C=0 && in\ [0,1]\times(0,T),\\
&\left(-\frac{1}{P_e}\frac{\partial C}{\partial z}+C\right)\Bigg|_{z=0}=\delta(t) && on\ (0.T),\\
&\frac{\partial C}{\partial z}\bigg|_{z=1}=0 && on\ (0,T),\\
&C|_{t=0}=0 && on\ (0,T),
\end{aligned}
\tag{2}
$$

Where $\mathcal{L}$ is the convection-diffusion-reaction operator

$$
\mathcal{L}=-\frac{1}{P_e}\frac{\partial^2}{\partial z^2}+\frac{\partial}{\partial z}+\mu I,
\tag{3}
$$

Where I denotes the identity operator. The equation (3) is discretized with respect to time using θ scheme and then a plain Galerkin Finite element discretization is applied.

In non-equilibrium models there are different sorption processes and can be classified into chemical non-equilibrium and physical non-equilibrium. The two regions transport model is based on the assumption that the dissolved phase can be partitioned into mobile and immobile phase. The dimensionless equations representing the non-equilibrium models are given as [50]

$$
\beta R\frac{\partial C_1}{\partial t}-\frac{1}{P_e}\frac{\partial^2 C_1}{\partial z^2}+\frac{\partial C_1}{\partial z}+w(C_1-C_2)+\mu_1 C_1=0.
\tag{4}
$$

$$
(1-\beta)R\frac{\partial C_2}{\partial t}-w(C_1-C_2)+\mu_2 C_2=0
\tag{5}
$$

Where the subscript 1 and 2 refer to the instantaneous and non-instantaneous adsorption sites for the chemical non-equilibrium model or mobile and immobile regions for physical non-equilibrium model; β is the partitioning coefficient between the two regions and *w* is the dimensionless mass transfer coefficient. The above equations (4) and (5) are further simplified with initial and boundary conditions and expressed as

$$\begin{cases} \beta R \dfrac{\partial}{\partial t} C_1 + \mathcal{L}_1 C_1 - w C_2 = 0 \quad in\ [0,1] \times (0,T), \\ (1-\beta) R \dfrac{\partial}{\partial t} C_2 + (w + \mu_2) C_2 - w C_1 = 0 \quad in\ [0,1] \times (0,T), \\ \left(-\dfrac{1}{P_e} \dfrac{\partial C_1}{\partial z} + C_1 \right) \Big|_{z=0} = \delta(t) \quad on\ (0.T), \\ \dfrac{\partial C_1}{\partial z} \Big|_{z=1} = 0 \quad on\ (0,T), \\ C_1|_{t=0} = 0 \quad on\ (0,T), \\ C_2|_{t=0} = 0 \quad on\ (0,T), \end{cases} \tag{6}$$

Where

$$\mathcal{L}_1 = -\frac{1}{P_e} \frac{\partial^2}{\partial z^2} + \frac{\partial}{\partial z} + (w + \mu_1) I \tag{7}$$

The model is solved using time discretization with θ scheme and then a plain Galerkin Finite element discretization.

Analytical solutions of one-dimensional solute transport problems with different initial and boundary conditions, in finite as well as semi-finite domain have been reported in the literature [51 ,52].

The CDE describing the one-dimensional convective -dispersive transport through a homogeneous medium with a linear and reversible equilibrium sorption and without degradation of the solute, under steady flow is given as [53]

$$R \frac{\partial C_1^{\tau *}}{\partial t} = D \frac{\partial^2 C_1^{\tau *}}{\partial x^2} - v \frac{\partial C_1^{\tau *}}{\partial x} \tag{8}$$

Where C_1^* is the solute normalised resident concentration in the liquid phase $(\frac{C_1^\tau}{C_0})$, C_1^τ is the resident concentration in the liquid phase at distance x and time t, C_0 is the input concentration, D is the effective diffusion-dispersion coefficient, v is the average pore-water velocity and R is the retardation factor. The analytical solution for equation (8) with flux -type inlet boundary conditions [54] expressed in terms of flux concentrations and cumulative drainage *(I)* is [54,55] is

$$C^{f*}(x,I) = \frac{1}{2} erfc\left[\frac{Rx - v'I}{2(D'RI)^{\frac{1}{2}}}\right] + \frac{1}{2} exp\left(\frac{v'x}{D'}\right) erfc\left[\frac{Rx + v'I}{2(D'RI)^{\frac{1}{2}}}\right] \quad (9)$$

The above equation can be used to calculate flux concentrations inside and at the exit boundary of the column. Here, $C^{f*}(x,I) = \frac{C^{f}(C,I)}{C_0}$ is the normalized flux concentration in the column at depth x and cumulative drainage *I(cm water),* $C^{f}(x,I)$ is the flux concentration, and *v'* (cm soil/cm water) and *D'* (cm^2 soil/cm water) are the solute velocity and diffusion-dispersion coefficient expressed in terms of cumulative drainage.

The convective lognormal transfer function model analytical solution corresponding to equation (9) is [56]

$$C^{f*}(x,I) = \frac{1}{2}\left\{1 + erf\left[\frac{ln\left(\frac{I\lambda}{RI_u x}\right) - \mu}{\sigma\sqrt{2}}\right]\right\} \quad (10)$$

Where I is divided by R to account for linear and reversible equilibrium sorption, I_u is a unit cumulative drainage so as to make logarithmic argument unitless, $\mu\ and\ \sigma$ are the CLT model parameters and λ is the calibration depth.

For a homogeneous column *V* and D are constant whereas in a heterogeneous field they vary with *x* and *y*. This variation is viewed as random because of uncertainty and the actual field is regarded as a realization of an ensemble of fields with the same probability distribution functions (PDF) of the variables of interest. So, in the stochastic approach [57]to study solute transport model the PDF of concentration for fixed *z* and *t* or the related cumulative probability:

$$P(z,t;C) = \int_0^A f(z,t;C)dC \quad (11)$$

where P is the probability that $C \leq A$ at depth z and time t. The cumulative probability distribution of *V* can be computed in a general method from

$$P(V) = \int dY \int f(R,Y) dR \tag{12}$$

Where $f(R,Y)$ is the joint probability density function of R, Y and the integration region in the double integral depends on V and Y.

The average concentration (C) over the field is given by

$$\bar{C}(z,t) = 1 - P(V) \tag{13}$$

Where $\bar{C}$ is the ratio between the area of the field for which $C = 1$ and the total area of the field. In the particular simple case of uniform transport Average Field Concentration $\bar{C}(z,t)$ is given by-

$$\bar{C} = 0.5\left[1 - \operatorname{erf}\frac{0.5\, In\, \xi - m_Y}{\sqrt{2}\sigma_Y}\right] for\ (\xi < r), \tag{14}$$

$$\bar{C} = 0.5\left[1 + \operatorname{erf}\frac{(0.5\omega)\, In(\xi r^{\omega-1}) - m_Y}{\sqrt{2}\sigma_Y}\right] for\ (\xi > r)$$

Where,

$$\xi = \frac{z\theta_s}{tK_s^*}, \qquad r = \bar{R}/K_s^*, \qquad and \qquad S_R = d_R/\bar{R} \tag{15}$$

which enable to calculate the value of $\bar{C}$ in terms of the dimensionless variables $\xi, r\ and\ S_R$ .For a spatially variable field a stochastic approximate model of transport is established [57].For this purpose, the expectation $E(C)$ and the variance σ_C^2 as a function of z and t are calculated from

$$E[C(z,t)] = \frac{1}{N}\sum_{i=1}^{N} C_i(z,t)$$

$$\sigma_C^2(z,t) = \frac{1}{N}\sum_{i=1}^{N}\{C_i(z,t) - E(C(z,t))\}^2$$

Most of the works [58, 59, 60, 61, 62] are based on assuming ideal conditions for porosity, seepage flow and dispersion. Some works [63, 64, 65, 66] includes the deviation in ideal conditions, due to adsorption, first order radio-active decay and/or chemical reactions. The study of uniform flow and unsteady flow against the dispersion in finite porous media were also undertaken [67,68]. A numerical model for one dimensional fluoride transport in unsaturated stratified soil considering the retardation factor and source sink term has been also presented [69].

The development of solute transport problems in two dimensions involve both longitudinal as well as transverse dispersion along with porous media flow in addition to advection. The literature is replete with numerous works on solutions of two, three-dimensional advection -diffusion equations [70 ,71 ,72,73,74,75]. A Laplace transform solution for tracer tests have been developed [76] developed assuming that advection and longitudinal dispersion are the transport mechanisms in a radially converging flow field.

An instantaneous and continuous point-source solution for a two-dimensional ADE model with constant, linear, asymptotic, and exponentially varying dispersion coefficients has also been developed [77].

Model for solute transport in rivers based on advection-dispersion equation for transport in the main channel with a sink term describing diffusive solute transfer to the hyporheic zone [78] has also been developed and the analytical solution of the system of equations so obtained was found for instantaneous injection of a conservative tracer in an infinite uniform river reach with steady flow [79].

Convective -dispersive equation (CDE) and Convective -lognormal transport (CLT) models were employed [80] to study fluoride retardation factor in unsaturated and undisturbed soil column. A numerical solution using finite difference technique was developed [81] for two-dimensional solute transport with periodic flow in homogeneous porous media. Analytical and numerical solutions for solute transport modelling in homogeneous semi-infinite porous medium with the variable temporally dependent boundary has been also studied [82]. Mathematical model for two-dimensional solute transport in a semi-infinite heterogeneous porous medium with spatially and temporally dependent coefficients for pulse type input concentration of varying nature has been developed [83].

The leaching kinetics of fluoride by loading AlF3 on undisturbed vertical saline soil columns were studied by [84] wherein saline soils from Sāmbhar region of Rajasthan was selected for the same. Linear relationship was established between the concentrations of leachable fluoride [F-]i and rate of leaching (LRobs). [F-] i and LRobs were found to decrease with increase in Na+ and Ca+2 levels of extractant, while an increase has been observed with increase in temperature and OH- ions. Maximum [F-]i are resulted with addition of NH4OH in percolating water and minimum with addition of KOH. Total leachable F- was found to be unaffected by incubation time. First Order model was found to be best fit for representing fluoride leaching in the present experimental conditions.

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Chapter 3

Mathematical Formulation and Solution for Fluoride Ion Transport in Soil

3.1 INTRODUCTION

The study of fluoride ion transport in soils is important for a number of reasons. Fluoride is an important micronutrient required for human and animal health. But it may be highly toxic particularly if present in high concentrations. Thus, fluoride becomes a pollutant if its concentration exceeds some prescribed water quality standard i.e. if it is greater than 1ppm as defined by WHO. The study of the fate of fluoride ion in soil and resultant pollution in soil and groundwater is vital for sustaining agricultural productivity and land utility.

The geological media between the land surface and the regional water table below is called the unsaturated zone or vadose zone [1]. The word “vadose” is derived from the Latin word *vadosus* meaning shallow [2] As per the definition, the vadose zone includes the crop root layer, the intermediate zone between the root layer and the capillary fringe above the saturated water table. It plays a vital role in the global hydrological cycle controlling surface water infiltration, runoff and evaporation and hence the availability of soil water and nutrients to plants. In recent years much more, attention has been focused on chemical transport in and through this zone [3,4]as a result of increased use of agrochemicals such as fertilizers and pesticides and increased demands to store and dispose of industrial and municipal wastes such as sewage. The vadose zone is usually the first subsurface environment to encounter surface applied agrochemicals and contaminants and hence all surface and subsurface chemical concentrations and subsequent environmental impacts are inextricably linked to the physical, biological and chemical dynamics including sorption-desorption, volatilization, photolysis and degradation [2].

Our current understanding of physical and chemical processes in the vadose zone results largely from more than 70 years of mathematical modeling of variably saturated flow using Richards' equation [5] coupled with the Fickian-based convection-dispersion equation for solute transport. Analytical and numerical solutions of these classical equations are widely used to study and predict water flow and solute transport for specific laboratory and field experiments and to extrapolate these results for other experiments in different soils, crops and climatic conditions.

The industries dealing with aluminium, steel, glass, and fertilizer are the main contributor to generation of fluoride wastes. When a great deal of fluoride pollutants is drained into the soil and the amount of pollutants exceeds the capacity of self-purification of the soil, pollutants will continue to leach downwards with water and pollute groundwater. Since Fluorine is reactive in nature, it infiltrates through the vadose zone and reach the water-table and continue to migrate in the direction of groundwater flow. Therefore, in order to avoid health risk, it is essential to understand the transport process of fluoride through the subsurface porous media. It is also crucial from the point of view of predicting and controlling the migration of fluoride in the soil-water system.

The process of transport of reactive contaminants through porous media has been represented by various mathematical models over the years [6, 7, 8]. 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 [9, 10, 11].

The transport of reactive chemicals in porous media undergoes various chemical changes through advection, diffusion and dispersion. In addition, it involves other mechanisms like rate-limited sorption and desorption, biodegradation, and chemical reaction. 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 [12]. The solution of transport equation considered reversible and irreversible solute adsorptions. The irreversible adsorption was represented by the sink/source term.

The solute transport process has been modelled using the soil water column experiment [13]. The present research study presents a mathematical model to study leaching kinetics of F- by loading KF on undisturbed vertical soil column of the soil collected from Sambhar region of Rajasthan [13].

3.2 EXPERIMENTAL BACKGROUND

In the soil column experiment [13] soil columns were prepared surrounded by glass jacket of continuously flowing thermostat water. 60 g soil of pH 8.2 and of particle size (53>r) was gently packed at water filled porosity 0.315 cm^3/cm^3.The leachate's pore volume was determined using equation (1) [14].

$$P_v = \frac{qt}{\theta V} \tag{1}$$

Where

q =Volume of effluent collected per unit time i.e. flow rate $cm^3\ h^{-1}$

t =Time that has elapsed since the slug was introduced

θ =Water filled porosity cm^3/cm^3

V =Total volume of soil column.

A schematic diagram of the soil column leaching experiment is shown below

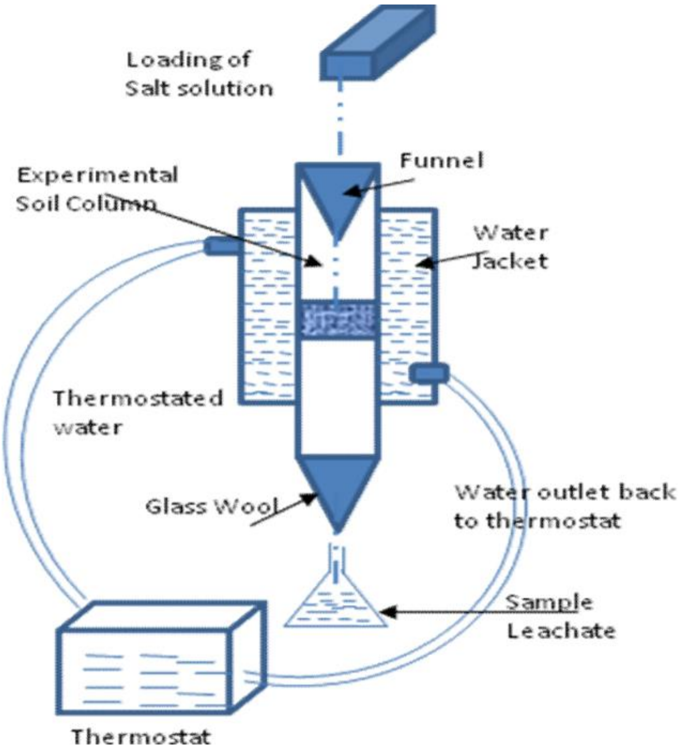

Fig. 1. Schematic diagram of column leaching [13]

In each experiment, a fixed volume of aqueous salt solution (slug) with desired anion concentration (KF) was added at the top of the soil column and was allowed to get adsorbed uniformly in the column for 24 hrs, after which the column was continuously leached with de-ionized water or with other extractant as per requirement of the study [13]. The flow rate of extractant measured was constant (2+0.5 ml/10 min). Till the soluble anions were completely removed, leaching was carried out. After which, the column soil was transferred into the beaker in a known volume of extractant and this salt solution was stirred for 2 hrs. The ion concentration was further determined in the filtrate of the soil suspension to ensure the complete removal of soluble ions from the soil in the column. The total leachable concentration was taken equal to the total leachable concentration present initially during leaching (i.e. concentration t=0). The concentration of ions was determined in leachate collected periodically at an interval of 2 min, during each kinetic run.

3.3 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

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

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, $\rho =$ soil bulk density, $z =$ is vertical coordinate measured vertically downwards, $t =$ is time in sec.

The course and persistence of the fluoride ion in the unsaturated and saturated zones is determined by its transformation process. The main among processes being microbiological degradation (biodegradation) and hydrolysis (chemical degradation). The microbiological decomposition of chemicals in the solution phase through enzymatically mediated reactions is biodegradation. The need of microorganism for energy, carbon, and other essential nutrients is the impetus for these decomposition reactions.

In hydrolysis the chemical speciation of an organic contaminant gets changed. In this, as a result of the reaction of the fluoride salt with water, an exchange of some functional group from the salt with a hydroxyl (OH^-) group takes place. The extent of fluoride ion contamination attenuation by both bio degradation and hydrolysis depends on the chemical properties of the contaminant as well as the aqueous medium. The transformation processes in present case is shown to be following first-order kinetic reactions [13]. In this study the k denotes the first-order rate constants of the fluoride ion.

The apparent dispersion coefficient, D, in Equation (2), represents the combined effects of molecular diffusion and mechanical dispersion (velocity-dependent). Therefore, D can be expressed as

$$D = D_m + \alpha|V|, \tag{3}$$

where $D_m =$ molecular diffusion coefficient dependent on the moisture content, $\theta; V = q/\theta =$ effective pore-water velocity; and $\alpha =$dispersivity. There is wide variation in dispersivity estimates for field and laboratory locations, which may be due to the non-homogeneous and anisotropic nature of the field flow system compared to homogeneous, isotropic conditions of laboratory tests [15].

The apparent dispersion coefficient given by equation (3) is appropriate for saturated and partially saturated flow conditions. The mechanical dispersion term is analogous to molecular diffusion in effect, but not in mechanism. The flow is assumed to be steady $(\partial\theta/\partial t = 0)$ and therefore equation (2) reduces to

$$\frac{\partial[F^-]}{\partial t} + \frac{\rho}{\theta}\frac{\partial(S)}{\partial t} = D\left\{\frac{\partial^2([F^-])}{\partial z^2}\right\} - \frac{q}{\theta}\frac{\partial[F^-]}{\partial z} - k[F^-]. \tag{4}$$

The above transport equation (4) takes into account the transport, adsorption, and transformation of fluoride ion. The term $k[F^-]$ in equation (4) represents the degradation of the parent fluoride salt to the first-step product.

The term S represents the concentration of the fluoride ion adsorbed to the soil. For simplification, we assume an existence of a local equilibrium and linear adsorption isotherm solution and adsorbed phases, then

$$S = K[F^-] \tag{5}$$

K is the distribution coefficient for the fluoride ion $[F^-]$ and therefore on differentiating equation (5) with respect to time *t*, we get

$$\frac{\partial S}{\partial t} = K\frac{\partial [F^-]}{\partial t} \tag{6}$$

Substituting the value of $\frac{\partial S}{\partial t}$ equation (6) in equation (4) and simplifying we get the following expression

$$\left(\frac{\rho K}{\theta} + 1\right)\frac{\partial [F^-]}{\partial t} = D\frac{\partial^2 [F^-]}{\partial z^2} - \frac{q}{\theta}\frac{\partial [F^-]}{\partial z} - k[F^-], \tag{7}$$

Or writing above equation (7) as

$$R\frac{\partial [F^-]}{\partial t} = D\frac{\partial^2 [F^-]}{\partial z^2} - V\frac{\partial [F^-]}{\partial z} - k[F^-], \tag{8}$$

where $R = 1 + \frac{\rho K}{\theta}$ known as the Retardation Factor and $V = \frac{q}{\theta}$ the pore water velocity. The retardation factor represents the extent to which the movement of the parent material or its metabolites are retarded relative to the water movement in the soil.

The initial and boundary conditions applied to equation (8) are

$$[F^-] = [F^-]_i \quad when\, t = 0, \qquad z \geq 0, \tag{9a}$$

$$[F^-] = \begin{cases} [F^-]_{ad} & 0 < t \leq t_0 \\ 0 & t > t_0 \end{cases}, \tag{9b}$$

$$\left.\frac{\partial [F^-]}{\partial z}\right|_{z=\infty} = 0. \tag{9c}$$

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 $t=t_0$.

3.4 ANALYTICAL SOLUTION

The analytical solutions [16,17] for the fluoride transport problem in semi-infinite column with a first order decay and zero order production are discussed here. Because of the relatively small imposed mathematical boundary conditions, the analytical solution for a semi-infinite system should provide close approximations to analytical solutions that are applicable to physical well-defined system, especially for laboratory columns that are not too short [18].

Now onwards writing fluoride ion concentration at any time t as C i.e. $[F^-]$. Thus equation (8) takes the form

$$\frac{R}{D}\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial z^2} - \frac{V}{D}\frac{\partial C}{\partial z} - \frac{k}{D}C. \qquad (10)$$

Here on representing initial concentration of fluoride ion i.e. $[F^-\,]_i$ as C_0 and pulse application of fluoride ion to the soil surface $[F^-\,]_{ad}$ as C_i (for a duration t_0).

Taking Laplace transform of equation (10), the following expression is obtained

$$\frac{d^2\bar{C}}{dz^2} - \frac{V}{D}\frac{d\bar{C}}{dz} - \frac{k}{D}\bar{C} = \frac{R}{D}[s\bar{C} - C(z,0)], \qquad (11)$$

Where,

$$\bar{C} = \bar{C}(z,s) = \int_0^\infty C(z,t)\exp(-st)dt. \qquad (12)$$

Substituting the value of $C(z,0) = C_0$ from equation (9a) in equation (11), the resultant expression obtained is

$$\frac{d^2\bar{C}}{dz^2} - \frac{V}{D}\frac{d\bar{C}}{dz} - \frac{Rs+k}{D}\bar{C} = -\frac{RC_0}{D}. \qquad (13)$$

Similarly taking Laplace transform of initial and boundary conditions (9b) and (9c), we get

$$\bar{C}(0,s) = \frac{C_i}{s}, \qquad (14a)$$

$$\frac{\partial \bar{C}}{\partial z} = 0 \ \ as \ \ z \to \infty. \tag{14b}$$

On solving equation (13), we obtain

$$\bar{C}(z,s) = C^1 \exp(rz) + C^2 \exp(r_1 z) + \frac{RC_0}{Rs+k}, \tag{15}$$

where

$$r = \frac{V}{2D} + \sqrt{\frac{V^2 + 4D(k+Rs)}{4D^2}} \tag{16a}$$

$$r_1 = \frac{V}{2D} - \sqrt{\frac{V^2 + 4D(k+Rs)}{4D^2}} \tag{16b}$$

Using equations (14a) and (14b) in equation (15) the values of C^1 and C^2 obtained are as follows

$$C^1 = 0, \tag{17}$$

$$C^2 = \frac{C_i}{s} - \frac{RC_0}{Rs+k}. \tag{18}$$

Thus, solution of equation (15) is given as

$$\bar{C}(z,s) = \left[\frac{C_i}{s} - \frac{RC_0}{Rs+k}\right] \exp(r_1 z) + \frac{RC_0}{Rs+k} \tag{19}$$

On taking inverse Laplace transform of equation (19) following solution as given by [18] is obtained

$$C(z,t) = \begin{cases} C_0 A(z,t) + C_i B(z,t) & 0 < t \le t_0 \\ C_0 A(z,t) + C_i B(z,t) - C_i B(z,t-t_0) & t > \ t_0 \end{cases}, \tag{20}$$

where

$$A(z,t) = e^{-\frac{kt}{R}}\left\{1 - \frac{1}{2} erfc\left[\frac{Rz - Vt}{2\sqrt{DRt}}\right] - \frac{1}{2} exp\left(\frac{Vz}{D}\right) erfc\left[\frac{Rz + Vt}{2\sqrt{DRt}}\right]\right\}, \tag{21}$$

and

$$B(z,t) = \frac{1}{2} exp\left[\frac{(V - U)z}{2D}\right] erfc\left[\frac{(Rz - Ut)}{2\sqrt{DRt}}\right] + \frac{1}{2} exp\left[\frac{(V + U)z}{2D}\right] erfc\left[\frac{(Rz + Ut)}{2\sqrt{DRt}}\right], \tag{22}$$

here

$$U = \sqrt{V^2 + 4kDR}. \tag{23}$$

3.5 NUMERICAL SOLUTION

The numerical model [19,20]is more preferable as it is easy to incorporate flexible boundary conditions as compared to the analytical solution. Here, an explicit finite-difference numerical technique is used to get the numerical solution of advective–dispersive transport equation including equilibrium sorption and first-order degradation for solute concentration in the solution phase. Applying the explicit scheme of finite difference method as by [21,22] to equation (8) and writing fluoride ion concentration at any time t as C i.e. $[F^-]$ the following approximation of the said equation (8) is obtained for an internal node *i*

$$R\frac{C_{i,j} - C_{i,j-1}}{\Delta t} = D\frac{C_{i-1,j-1} - 2C_{i,j-1} + C_{i+1,j-1}}{\Delta z^2} - V\frac{C_{i+1,j-1} - C_{i-1,j-1}}{2\Delta z} - kC_{i,j} \tag{24}$$

i-1 represents a known spatial level, *j* and *j-1* represent the time levels, Δz represents the grid size along the travel distance, and Δt represents the time interval.

Simplifying equation (24) the following expression is obtained,

$$\left[1+\frac{k\Delta t}{R}\right]C_{i,j} = C_{i,j-1}\left[1-\frac{2D\Delta t}{R\Delta z^2}\right] + C_{i-1,j-1}\left[\frac{D\Delta t}{R(\Delta z)^2}+\frac{V\Delta t}{2R\Delta z}\right] + C_{i+1,j-1}\left[\frac{D\Delta t}{R(\Delta z)^2}-\frac{V\Delta t}{2R\Delta z}\right] \tag{25}$$

For equation (25) to be stable

$$\left[1-\frac{2D\Delta t}{R(\Delta z)^2}\right] \geq 1 \quad and \quad \left[\frac{D\Delta t}{R(\Delta z)^2}-\frac{V\Delta t}{2R\Delta z}\right] \geq 0 \tag{26}$$

The system of linear equations so obtained were solved using Gauss –Jordan Method. The values of Δz were taken in consonance with equation (26). The temporal $[F^-]$ concentration profile for fluoride transport through the soil column has been shown in figures below. The numerical and analytical results of concentration profiles of $[F^-]$ have been compared with experimental results and verified.

3.6 RESULTS AND DISCUSSION

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 [13]

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	$0.00296/sec$
L	Length of Soil Column	$60 cm$

The leaching profiles in Fig. 2,3,4,5,6,7 represent the plotted graph between time and the $[F^{-}]_{l}$ that is leachable fluoride remaining at time t in the soil column at different values of $[F^{-}]_{ad}$. In the laboratory experiment [13] the fluoride source is supplied for predefined time t_0(24 hrs) that is it has a finite pulse source. The pore volume and relative concentration profile for leached $[F^{-}]$concentration in Fig. 8,9,10,11,12, and 13 have been predicted for column Peclet number $P_e = 2$ and Retardation factor $R = 15$.The column Peclet number is expressed as $P_e = \frac{VL}{D} = 2$ where V= pore velocity; L= column length= 60 cm; D= dispersion coefficient.

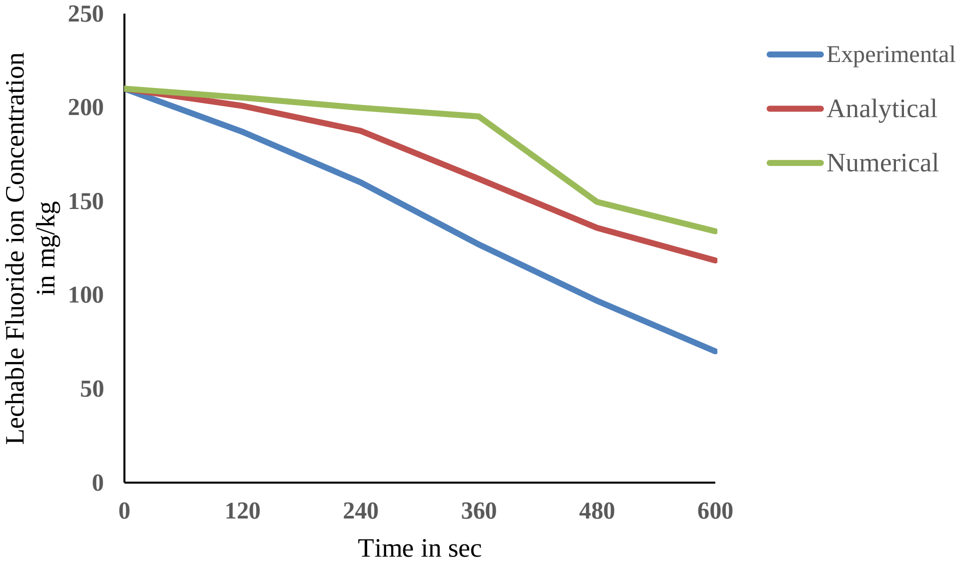

Fig.2 Leachable Fluoride ion concentration vs time when $[F^{-}]_{ad}$ =0 mg/kg

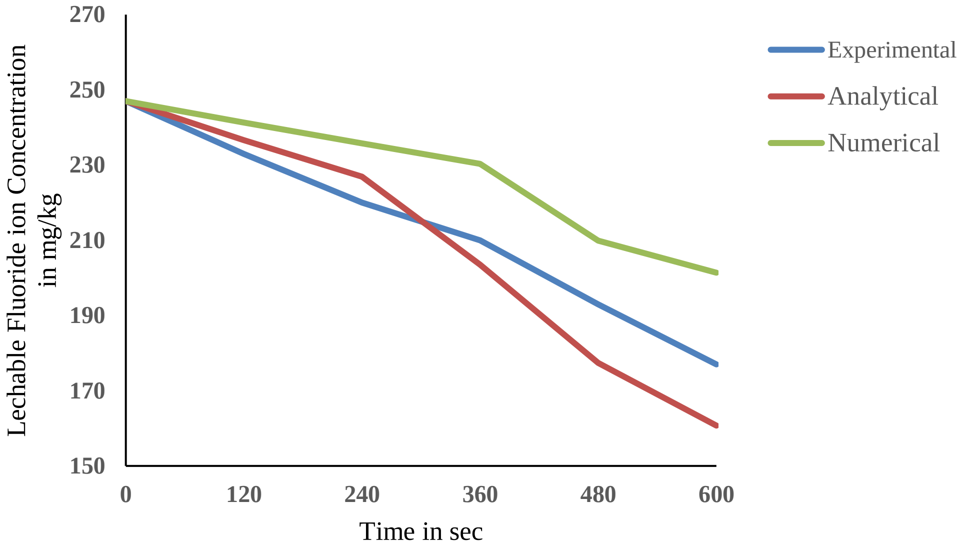

Fig.3 Leachable Fluoride ion concentration vs time when $[F^{-}]_{ad}$ =166 mg/kg

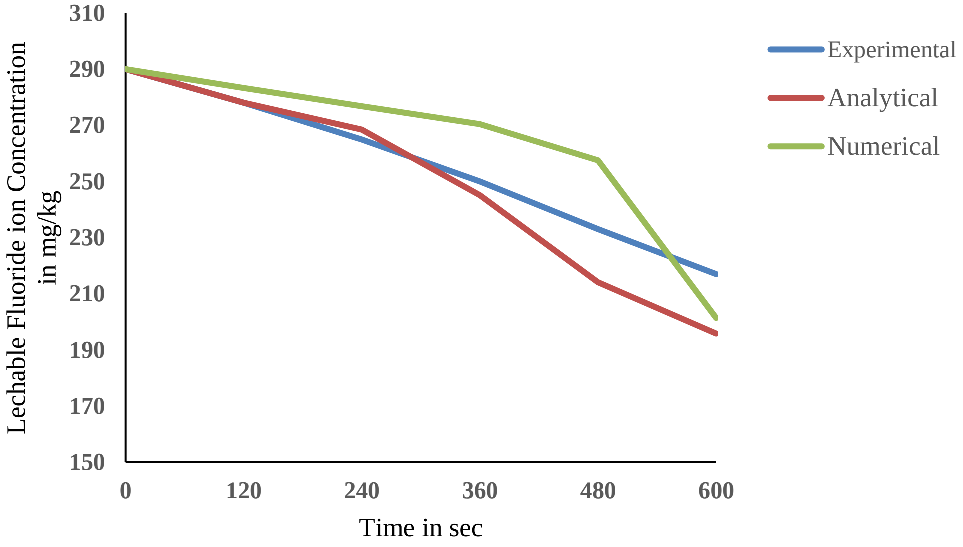

Fig.4 Leachable Fluoride ion concentration vs time when $[F^{-}]_{ad}$ =250mg/kg

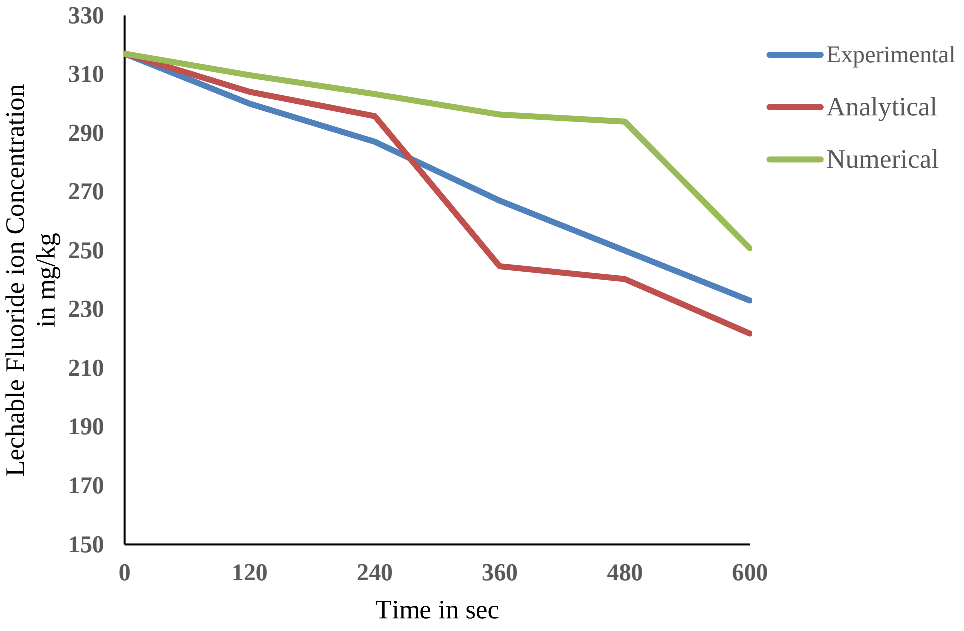

Fig.5 Leachable Fluoride ion concentration vs time when $[F^{-}]_{ad}$ =333mg/kg

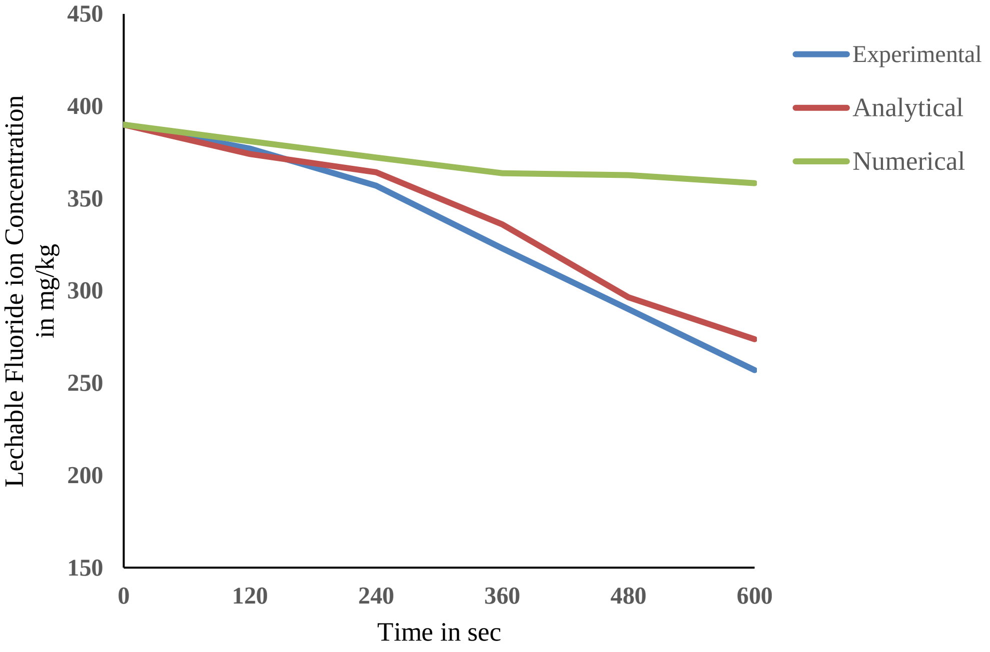

Fig.6 Leachable Fluoride ion concentration vs time when $[F^{-}]_{ad}$ =417mg/kg

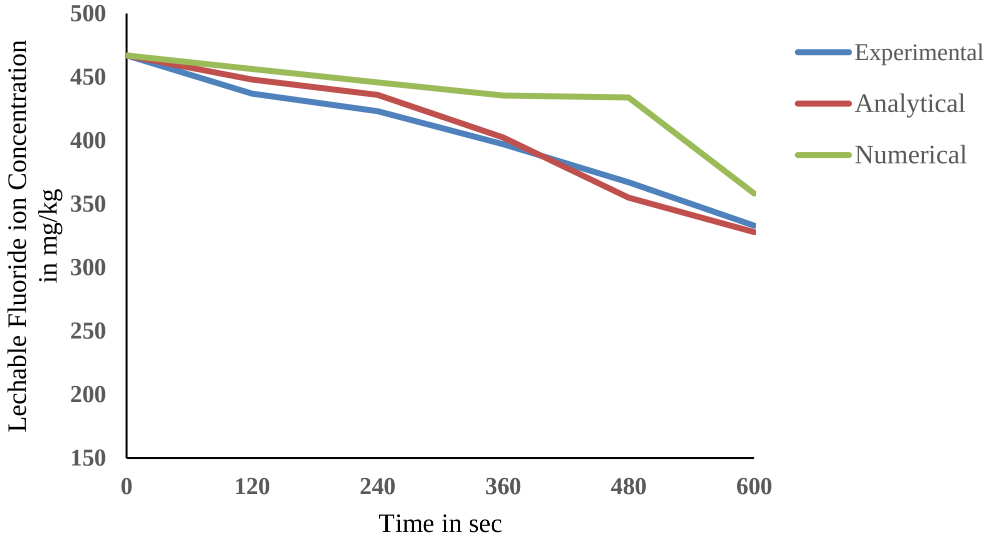

Fig.7 Leachable Fluoride ion concentration vs time when $[F^{-}]_{ad}$ =500mg/kg

The pore volume and relative concentration profiles for leached $[F^{-}]$concentration is shown in Fig.8,9,10,11,12,13 for different values of $[F^{-}]_{ad}$.

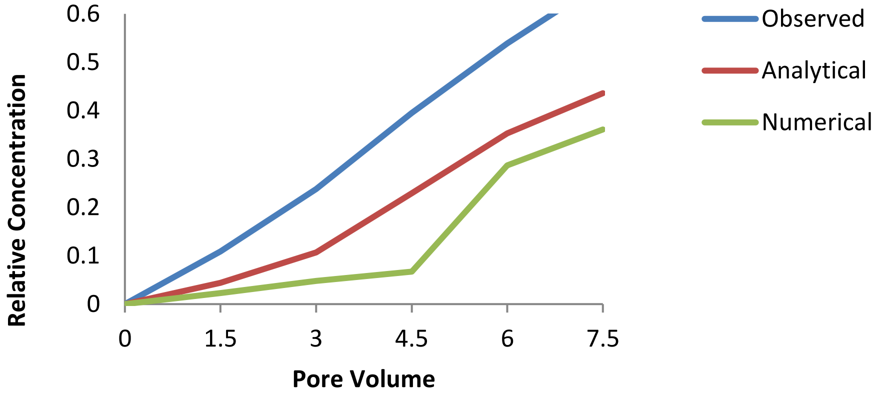

Fig.8 Pore Volume vs Relative Concentration of Leached Fluoride ion when $[F^{-}]_{ad}$ =0 mg/kg

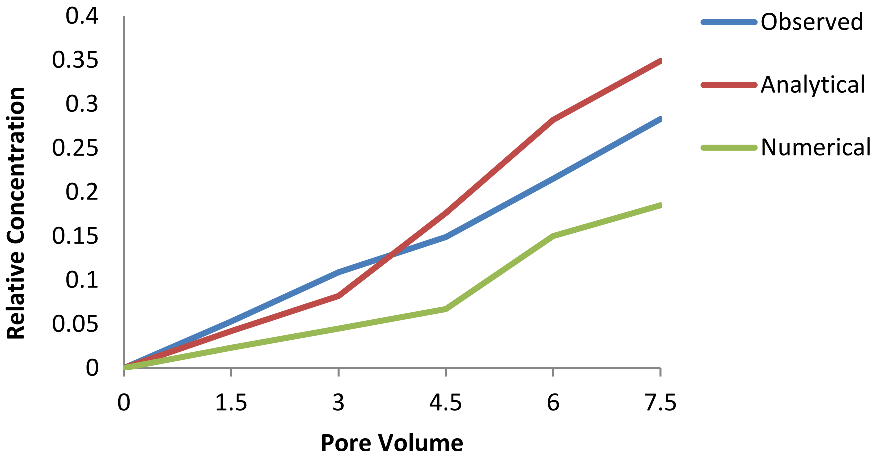

Fig.9 Pore Volume vs Relative Concentration of Leached Fluoride ion when $[F^{-}]_{ad}$ =166 mg/kg

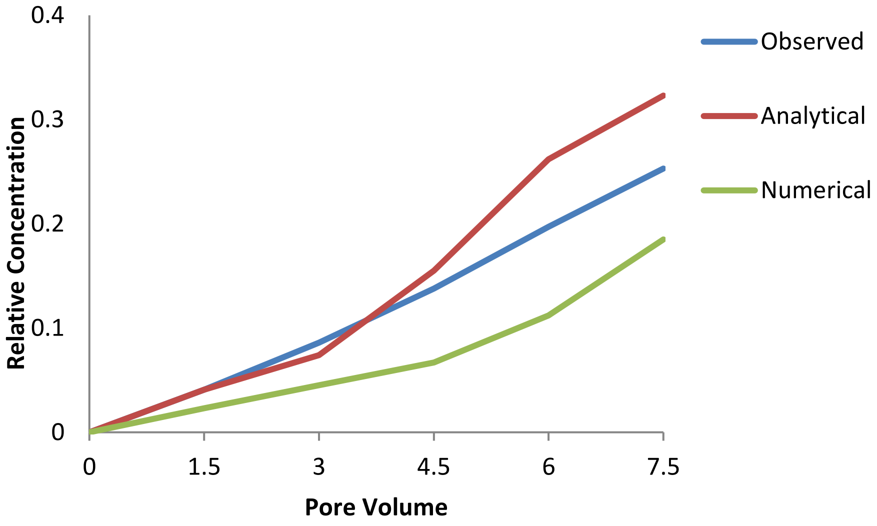

Fig.10 Pore Volume vs Relative Concentration of Leached Fluoride ion when $[F^{-}]_{ad}$ =250 mg/kg

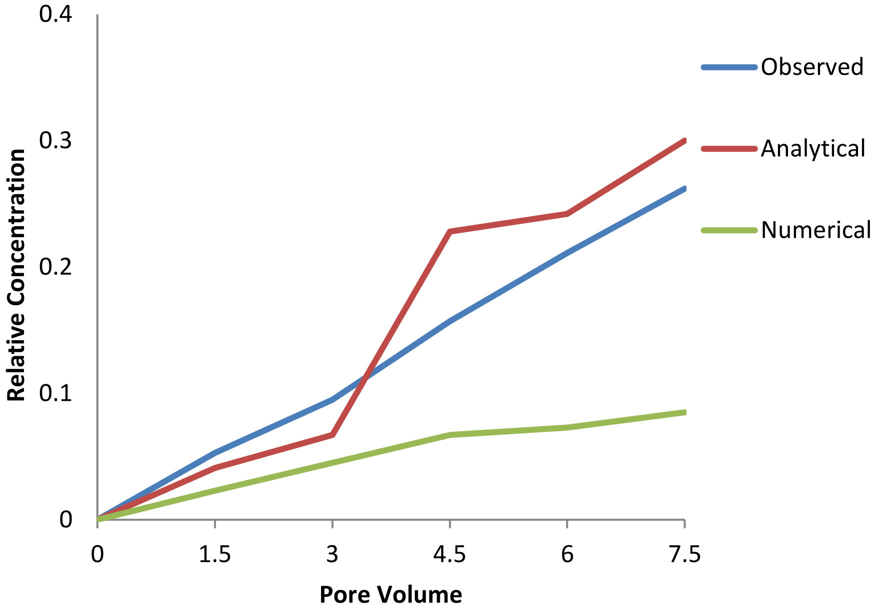

Fig.11 Pore Volume vs Relative Concentration of Leached Fluoride ion when $[F^-]_{ad}$ =333 mg/kg

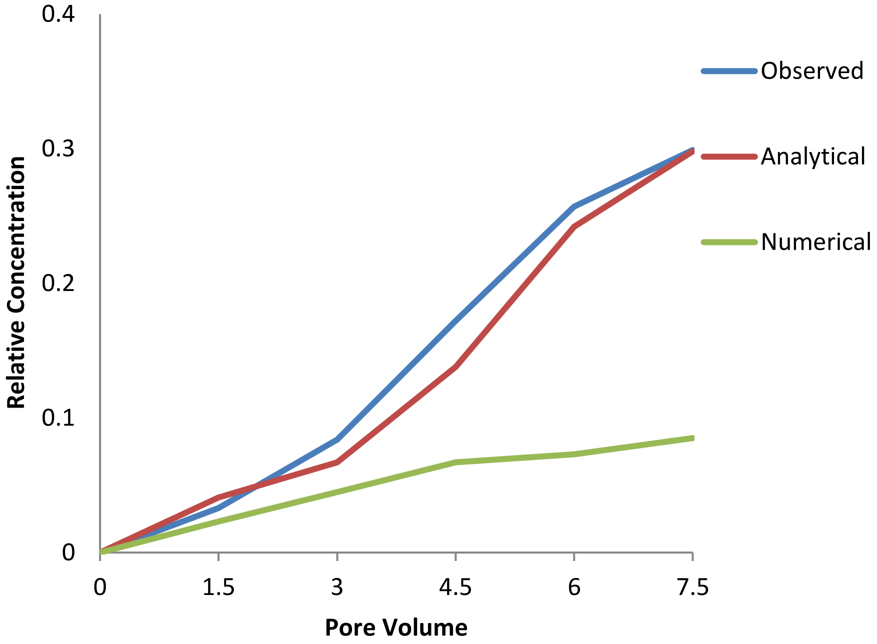

Fig.12 Pore Volume vs Relative Concentration of Leached Fluoride ion when $[F^-]_{ad}$ =417 mg/kg

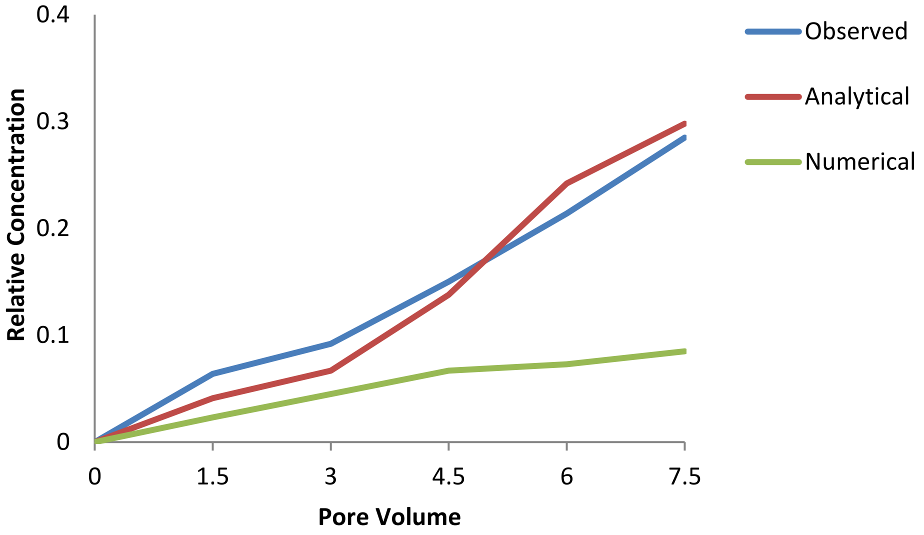

Fig.13 Pore Volume vs Relative Concentration of Leached Fluoride ion when $[F^{-}]_{ad}$ =500 mg/kg

3.7 CONCLUSION

Experimental, analytical and numerical results of BTCs have been presented for fluoride ion transport 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. The paper demonstrates that the combination of multicomponent chemistry, diffusion-limited sorption and transport can be modelled by combining mechanistic process descriptions. There were often more influencing factors than initially anticipated, even in relatively simple systems. Nevertheless, mechanistic modelling provides valuable insights into the processes that are involved in transport of fluoride in soil systems. From the graphs it is clear that analytical results are more comparable to observed results as compared to the numerical results. The numerical simulation also exhibits a fair comparison of the observed and simulated values.

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Chapter 4

Two-Dimensional Model for Fluoride Ion Transport in Soil for Steady flow

4.1 INTRODUCTION

Fluoride occurring naturally in the earth's crust in the form of rocks, coal, clay, and soil is released into the environment via the natural process of weathering of minerals, in emissions from volcanic ash and in marine aerosols [1]. Other anthropogenic sources causing deposition of Fluoride into soil are both direct through phosphate fertilizers or indirect through atmospheric pollution from industrial activities and burning of fossil fuels [2]. In areas without natural phosphate or fluoride deposits, the total fluoride concentrations in soils range from 20 to 1,000 μg/g, whereas the concentration in organic soils are usually lower [3 ,4].

Fluoride is a micro nutrient required for dental and skeletal growth of mammals. At the same time, it is also one of the most important environmental micro pollutants responsible for soil and groundwater pollution causing dental and skeletal fluorosis [5,6,7]. The concentration of fluoride that occurs in groundwater and the rate by which fluoride migrates to groundwater are the key factors determining the risk for human health and the environment. Both these processes are strongly influenced by the interaction of dissolved fluoride with the soil solid phase via adsorption and desorption [8] and cation-anion exchange. Therefore, it is important to study the migration and transport of fluoride ion in soil.

The development of mathematical models is an integral component of any effort to understand and predict the transport phenomena of fluoride migration and its persistence in soil and groundwater. The attention to prevent, reduce and eliminate soil and groundwater pollution has been growing with the growing importance of groundwater resources and the models are helpful tools to design and implement soil and crop management practises which minimize soil and water contamination.

Over the years, various mathematical models for the process of transport of reactive contaminants through porous media have been developed [9, 10, 11] based on advection diffusion equation. The advection diffusion equation is parabolic second order partial differential equation built on the basis of conservation of mass and Fick’s first law of diffusion.

Analytical solutions of one-dimensional solute transport problems with different initial and boundary conditions, in finite as well as semi-finite domain have been reported in the literature [12 ,13].

Most of the works [14 ,15 ,16,17and 18] are based on assuming ideal conditions for porosity, seepage flow and dispersion. Some works [19, 20 ,21 ,22] includes the deviation in ideal conditions, due to adsorption, first order radio-active decay and/or chemical reactions. The study of uniform flow and unsteady flow against the dispersion in finite porous media were also undertaken [23,24]. A numerical model for one dimensional fluoride transport in unsaturated stratified soil considering the retardation factor and source sink term has been also presented [25].

The development of solute transport problems in two dimensions involve both longitudinal as well as transverse dispersion along with porous media flow in addition to advection. The literature is replete with numerous works on solutions of two, three-dimensional advection -diffusion equations [26 ,27 ,28,29,30,31]. A Laplace transform solution for tracer tests have been developed [32] developed assuming that advection and longitudinal dispersion are the transport mechanisms in a radially converging flow field.

An instantaneous and continuous point-source solution for a two-dimensional ADE model with constant, linear, asymptotic, and exponentially varying dispersion coefficients has also been developed [33].

Model for solute transport in rivers based on advection-dispersion equation for transport in the main channel with a sink term describing diffusive solute transfer to the hyporheic zone [34] has also been developed and the analytical solution of the system of equations so obtained was found for instantaneous injection of a conservative tracer in an infinite uniform river reach with steady flow [33].

Convective -dispersive equation (CDE) and Convective -lognormal transport (CLT) models were employed [35] to study fluoride retardation factor in unsaturated and undisturbed soil column. A numerical solution using finite difference technique was developed [36] for two-dimensional solute transport with periodic flow in homogeneous porous media. Analytical and numerical solutions for solute transport modelling in homogeneous semi-infinite porous medium with the variable temporally dependent boundary has been also studied [37]. Mathematical model for two-dimensional solute transport in a semi-infinite heterogeneous porous medium with spatially and temporally dependent coefficients for pulse type input concentration of varying nature has been developed [38].

In our earlier chapter one dimensional advection -dispersion equations were developed to represent fluoride ion leaching and analytical and numerical solutions were obtained. On comparing the analytical and experimental values it is found that the analytical solution offers a good comparison to the observed values. One dimensional model takes into account the flow or contamination of fluoride only in longitudinal direction that is downwards. In the present paper a two-dimensional advection-dispersion model fluoride transport in soil is presented in which, the transverse component of velocity and dispersion coefficients are also considered along with the longitudinal components. The longitudinal and transverse seepage velocities are taken to be constant. The properties of soil column experiment are extended here also and therefore in the model we assume the soil medium to be homogeneous, isotropic saturated and of semi-infinite in horizontal plane. Since fluoride is reactive in nature and has the tendency to get adsorbed in the medium retardation factor and a first order decay term as a constant is also considered.

A pulse type boundary condition is assumed which is in consonance with the realistic situation in the sense that generally industries or waste sites release pollution in a finite period or pesticides containing fluorides are applied for a certain duration of time with the awareness of the pollution or government regulation. Analytical solution is obtained for a fixed initial concentration with the help of Laplace transformation technique.

4.2 MATHEMATICAL FORMULATION OF THE PROBLEM

The soil medium has been assumed to be a homogeneous and isotropic porous medium that is having same water content, bulk density and retention factor. The fluorides find their way into the soil subsurface predominantly by advection, that is by flow of groundwater, and by dispersion which is caused by mechanical mixing and molecular diffusion. Due to small seepage velocity molecular diffusion is neglected.

Assuming that the fluoride is introduced in to the soil system in the form of pulse i.e. for a time $t_0 > t$, *the* distance in downward direction i.e. longitudinal direction be represented by x [L] and the distance in horizontal i.e. lateral direction be represented by y [L]. The two-dimensional advection-diffusion equation is given as

$$R\frac{\partial C}{\partial t} = D_x\frac{\partial^2 C}{\partial x^2} + D_y\frac{\partial^2 C}{\partial y^2} - u\frac{\partial C}{\partial x} - v\frac{\partial C}{\partial y} - kC. \tag{1}$$

Here $C = C(x, y, t)$ = concentration of fluoride at any time t; D_x [LT^{-2}] =Dispersion coefficient along longitudinal direction; D_y [LT^{-2}] = Dispersion coefficient along transverse direction;

u[LT^{-1}] = uniform constant velocity along x or longitudinal direction and v[LT^{-1}] = uniform constant velocity along y or transverse direction; R= retardation factor (dimensionless); k= degradation constant.

The dispersion coefficient is proportional to a power of the seepage velocity which ranges between 1 and 2 [39]. In India, the experimental observation has shown that the dispersion is directly proportional to the seepage velocity with a power ranging from 1 to 1.2 [40] and is applicable to various porous media. In present study dispersion is assumed to be directly proportional to the seepage velocity. Therefore,

$$D_x = au \ \ and \ D_y = bv, \qquad (2)$$

where a and b are the coefficients having the dimensions [L] and depends upon pore geometry and average pore size diameter of the porous medium. The source of fluoride contamination is taken to be uniform pulse-type point source that is, it is introduced into the porous medium continuously at a uniform rate up to a certain time period i.e. t_0 and for $t >$ t_0 it becomes zero. The porous medium is considered to be having some inherent initial concentration of fluoride C_i. Flux type homogeneous conditions are assumed at far ends of the medium, along both the directions. So, writing initial and boundary conditions mathematically

$$C(x,y,t) = C_i \ \ ; \quad x \geq 0, y \ \geq 0 \ , t = 0. \qquad (3)$$

$$C(x,y,t) = \begin{cases} C_0 \, ; & 0 < t \leq t_0 \\ 0 \ \ ; & t \geq t_0 \end{cases}, \qquad (4a)$$

$$\frac{\partial C}{\partial x} = 0 \, ; \, \frac{\partial C}{\partial y} = 0 \, ; x \to \infty, y \to \infty, t \geq 0. \qquad (4b)$$

4.3 ANALYTICAL SOLUTION

The problem of fluoride transport modelling in homogeneous porous medium can be solved using numerical, analytical, statistical, finite element method etc. It has been observed that the analytical approach is more significant to estimate the pattern of solute concentration and various transport parameters from field data [40,41]. Also, in the earlier chapter for one dimensional model, the analytical solution shows more comparison with observed experimental values.

Introducing a new space variable

$$z = x + y\sqrt{\frac{D_y}{D_x}}. \tag{5}$$

Using equation (5) in equation (1), the resultant equation obtained is

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - U\frac{\partial C}{\partial z} - kC, \tag{6}$$

where,

$$D = D_x\left(1 + \frac{D_y^2}{D_x^2}\right), \tag{7}$$

and

$$U = u + v\sqrt{\frac{v}{u}}. \tag{8}$$

Using the new space variable *z*, the initial condition given by equation (3) and the boundary conditions given by (4a), (4b) are written as

$$C(z,t) = C_i \quad ; \quad z \geq 0, t = 0. \tag{9}$$

$$C(z,t) = \begin{cases} C_0\,; & 0 < t \leq t_0 \\ 0 \;\; ; & t \geq 0 \end{cases}, \tag{10a}$$

$$\frac{\partial C}{\partial z} = 0\,;\; z \to \infty, t \geq 0. \tag{10b}$$

Now, in order to solve equation (6), the following transformation is introduced which removes the convective term $U\frac{\partial C}{\partial z}$:

$$C(z,t) = K(z,t)exp\left\{\frac{Uz}{2D} - \frac{1}{R}\left(\frac{U^2}{4D} + k\right)t\right\} \tag{11}$$

The terms $\frac{\partial c}{\partial t}, \frac{\partial c}{\partial z}$ and $\frac{\partial^2 c}{\partial z^2}$ found from equation (11) to be used in equation (6) are as follows:

$$\frac{\partial C}{\partial t} = exp\left\{\frac{Uz}{2D} - \frac{1}{R}\left(\frac{U^2}{4D} + k\right)t\right\}\left\{\frac{\partial K}{\partial t} - \frac{K}{R}\left(\frac{U^2}{4D} + k\right)\right\}, \tag{12}$$

$$\frac{\partial C}{\partial z} = exp\left\{\frac{Uz}{2D} - \frac{1}{R}\left(\frac{U^2}{4D} + k\right)t\right\}\left\{\frac{\partial K}{\partial z} + \frac{UK}{2D}\right\}, \tag{13}$$

$$\frac{\partial^2 C}{\partial z^2} = exp\left\{\frac{Uz}{2D} - \frac{1}{R}\left(\frac{U^2}{4D} + k\right)t\right\}\left\{\frac{\partial K}{\partial t} - \frac{K}{R}\left(\frac{U^2}{4D} + k\right)\right\}. \tag{14}$$

Substituting the values from equation (12), (13) and (14) in equation (6) and simplifying the equation obtained is

$$R\frac{\partial K}{\partial t} = D\frac{\partial^2 K}{\partial z^2}. \tag{15}$$

As a result of the transformation used, given by equation (11), the initial condition and the boundary conditions given by equation (9) and (10a), (10b) respectively get transformed to

$$K(z,t) = C_i exp\left\{-\frac{Uz}{2D}\right\} \quad ; \quad z \geq 0, t = 0. \tag{16}$$

$$K(z,t) = \begin{cases} C_0 exp\left\{\frac{1}{R}\left(\frac{U^2}{4D} + k\right)t\right\} ; & 0 < t \leq t_0 \\ 0 \ ; & t \geq 0 \end{cases}, \tag{17a}$$

$$\frac{\partial K}{\partial z} + \frac{UK}{2D} = 0 \ ; \ z \to \infty, t \geq 0 \tag{17b}$$

Applying the Laplace transform to equation (15), (17a) and (17b) the expression obtained is

$$\frac{d^2\overline{K}}{dz^2} - \frac{Rs}{D}\overline{K} = -\frac{R}{D}\left[C_i exp\left(-\frac{Uz}{2D}\right)\right]. \tag{18}$$

$$\overline{K}(z,s) = \frac{C_0}{\left\{s - \frac{1}{R}\left(\frac{U^2}{4D} + k\right)\right\}}\left[1 - exp\left\{s - \frac{1}{R}\left(\frac{U^2}{4D} + k\right)\right\}t_0\right] \ ; z = 0, \tag{19a}$$

$$\frac{\partial \overline{K}}{\partial z} + \frac{U\overline{K}}{2D} = 0\ ;\ z \to \infty. \tag{19b}$$

where

$$\overline{K} = \int_0^\infty \mathrm{K(z,t)exp}(-st)dt \tag{20}$$

s = parameter.

On solving equation (18) the general solution of the differential equation is given as

$$\overline{K}(z,s) = C_1 \exp\left(\sqrt{\frac{Rs}{D}}z\right) + C_2 \exp\left(-\sqrt{\frac{Rs}{D}}z\right) + C_i \frac{exp\left(-\frac{Uz}{2D}\right)}{\left(s - \frac{U^2}{4RD}\right)}. \tag{21}$$

Where C_1 and C_2 are arbitrary constants whose values are to be determined using equations (19a) and (19b).

As a result, the values of these constants as obtained is

$$C_1 = 0\ ;\ C_2 = \frac{C_0}{\left\{s - \frac{1}{R}\left(\frac{U^2}{4D} + k\right)\right\}}\left[1 - exp\left\{s - \frac{1}{R}\left(\frac{U^2}{4D} + k\right)\right\}t\right] + C_i\,\frac{exp\left(-\frac{Uz}{2D}\right)}{\left(s - \frac{U^2}{4RD}\right)} \tag{22}$$

Substituting the above obtained values of C_1 and C_2 in equation (21), the final expression obtained is

$$\bar{K}(z,s) = \frac{C_0}{\left\{s - \frac{1}{R}\left(\frac{U^2}{4D} + k\right)\right\}}\left[1 - exp\left\{s - \frac{1}{R}\left(\frac{U^2}{4D} + k\right)\right\}\right] t\ \exp\left(-\sqrt{\frac{Rs}{D}}z\right) - C_i\,\frac{exp\left(-\frac{Uz}{2D}\right)}{\left(s - \frac{U^2}{4RD}\right)} exp\left(-\sqrt{\frac{Rs}{D}}z\right) + C_i\,\frac{exp\left(-\frac{Uz}{2D}\right)}{\left(s - \frac{U^2}{4RD}\right)}. \tag{23}$$

Taking inverse Laplace transformation to equation (23) and resubstituting for *K (z, t)*, we get

$$C(z,t) = C_0F(z,t) + C_iF_1(z,t);\quad 0 < t \le t_0, \tag{24a}$$

$$C(z,t) = C_0F(z,t) - C_0F(z,t-t_0) + C_iF_1(z,t);\quad t > t_0, \tag{24b}$$

Where

$$F(z,t) = \frac{1}{2}exp\left[\frac{\left(U - \sqrt{U^2 + 4kD}\right)z}{2D}\right] erfc\left[\frac{\left(Rz - \sqrt{U^2 + 4kD}\ t\right)}{2\sqrt{RDt}}\right] + \frac{1}{2}exp\left[\frac{\left(U + \sqrt{U^2 + 4kD}\right)z}{2D}\right] erfc\left[\frac{\left(Rz + \sqrt{U^2 + 4kD}\ t\right)}{2\sqrt{RDt}}\right], \tag{25a}$$

and

$$F_1(z,t) = \exp\left(-\frac{kt}{R}\right)\left[1 - \frac{1}{2}erfc\left\{\frac{Rz - Ut}{\sqrt{2DRT}}\right\} - \frac{1}{2}exp\left(\frac{Uz}{D}\right)erfc\left\{\frac{Rz + Ut}{\sqrt{2DRT}}\right\}\right] \quad (25b)$$

4.4 RESULTS AND DISCUSSION

In order to understand the concentration distribution of fluoride ion in soil the concentration values obtained from the analytical solution equation (24a) in the presence of initial fluoride concentration are discussed graphically for a chosen set of numerical values of the different variables.

Taking initial concentration of fluoride as C_i =0.05 and C_0 =1.0, where C_0 is the concentration of the pulse type source, where source is present for time t_0=5 hrs. The distances in longitudinal and transverse direction are taken to be $0 \leq x \leq 5$ and $0 \leq y \leq 5$, in meters respectively.

In actual field like situations the dispersion or flow of fluoride in longitudinal direction will be faster than in transverse direction due to presence of gravitational force in the former direction. Taking this into account the lateral velocity and dispersion coefficients are considered one- tenth of that in longitudinal direction.

The seepage velocity and the dispersion coefficients in longitudinal and transverse direction are as follows:

u=0.75 m/day; v= 0.075 m/day; D_x *=0.95* m^2*/day;* D_y *=0.95* m^2*/day; k= 0.02/day.*

Figure 1 and 2 show the concentration profiles for *t=4hrs and R=1.5 and t=2hrs and R=1.5.* The initial value of fluoride concentration profile is 1 for both the cases except that it is lower for smaller time and higher for larger time.

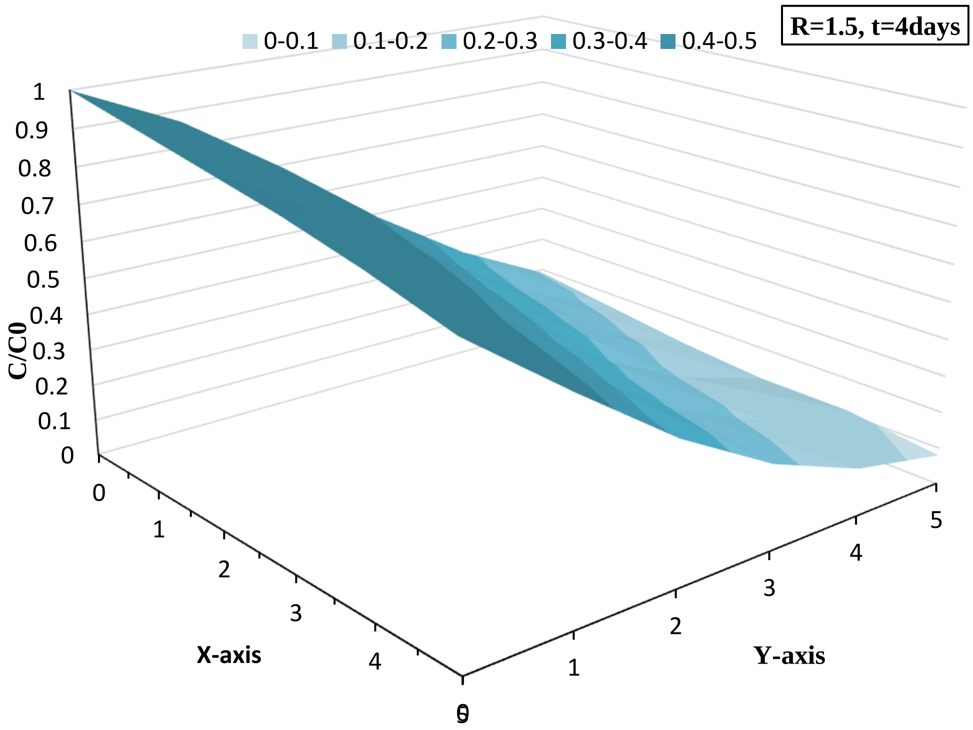


Figure.1 Concentration profiles of fluoride for steady flow for t=4days(t<t_0) and R=1.5

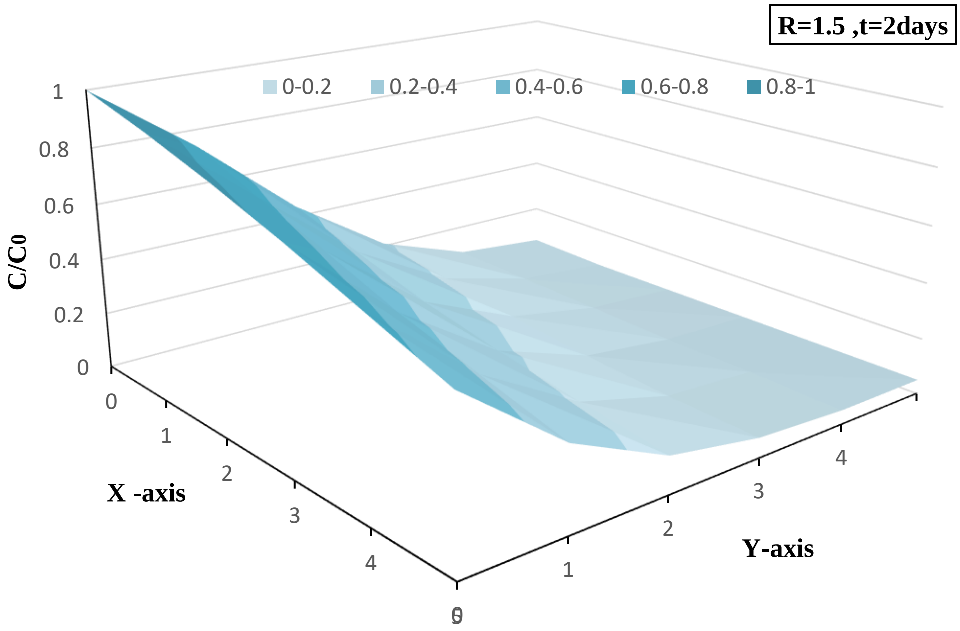


Figure.2 Concentration profiles of fluoride for steady flow for t=2days(t<t_0) and R=1.5

Figure .3 represents the concentration profile for t=4hrs and different value of retardation coefficient namely R =1.2 and on comparing with figure .1 it is observed that the concentration profile is lower for higher and higher for lower retardation factor.

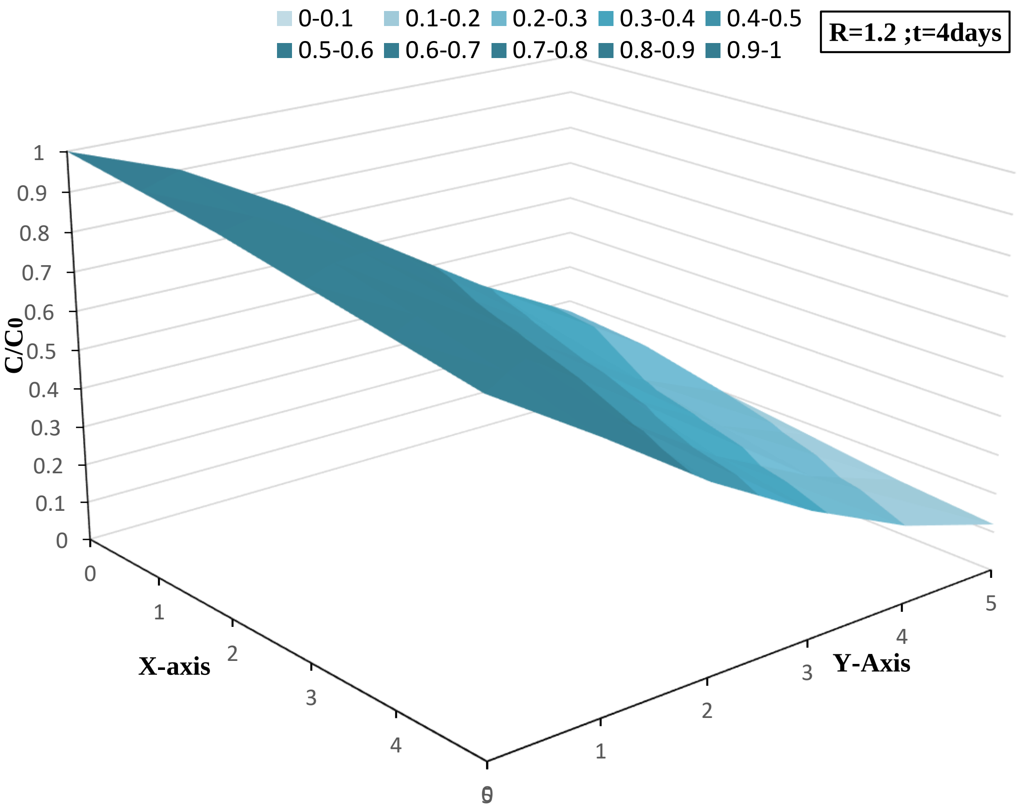


Figure.3 Concentration profiles of fluoride for steady flow for t=4days ($t<t_0$) and R=1.2

In figure .4 the fluoride concentration profile has been presented for a higher longitudinal and transverse dispersion coefficient namely $D_x =1.65\ m^2/day$ *and* $D_y =0.165\ m^2/day$ and on comparison with figure.1, it is observed that the concentration levels are lower for lower and higher for higher dispersion coefficient.

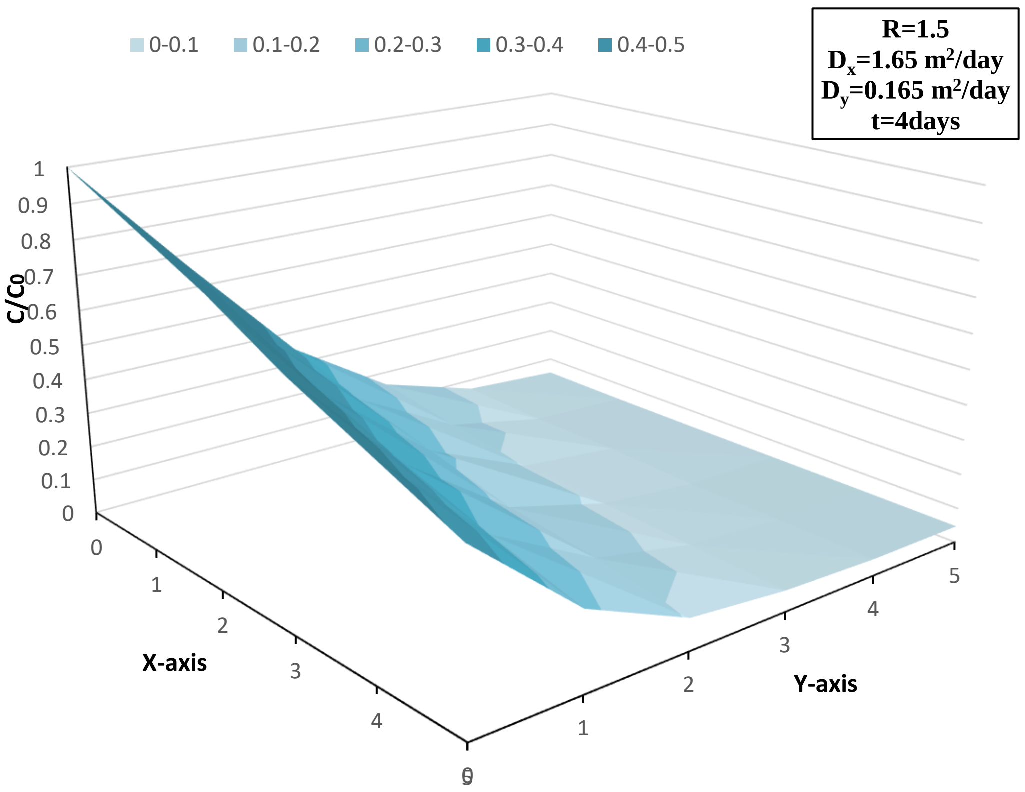


Figure.4 Concentration profiles of fluoride for steady flow for t=4days($t<t_0$) and R=1.5 for higher Dispersion coefficient

Figure. 5,6,7 and 8 represent fluoride concentration profile for the time $(t > t_0)$ when the source has been removed and is no longer present at the boundary. The values of seepage velocity and dispersion coefficients in both longitudinal and transverse directions have been taken as stated earlier.

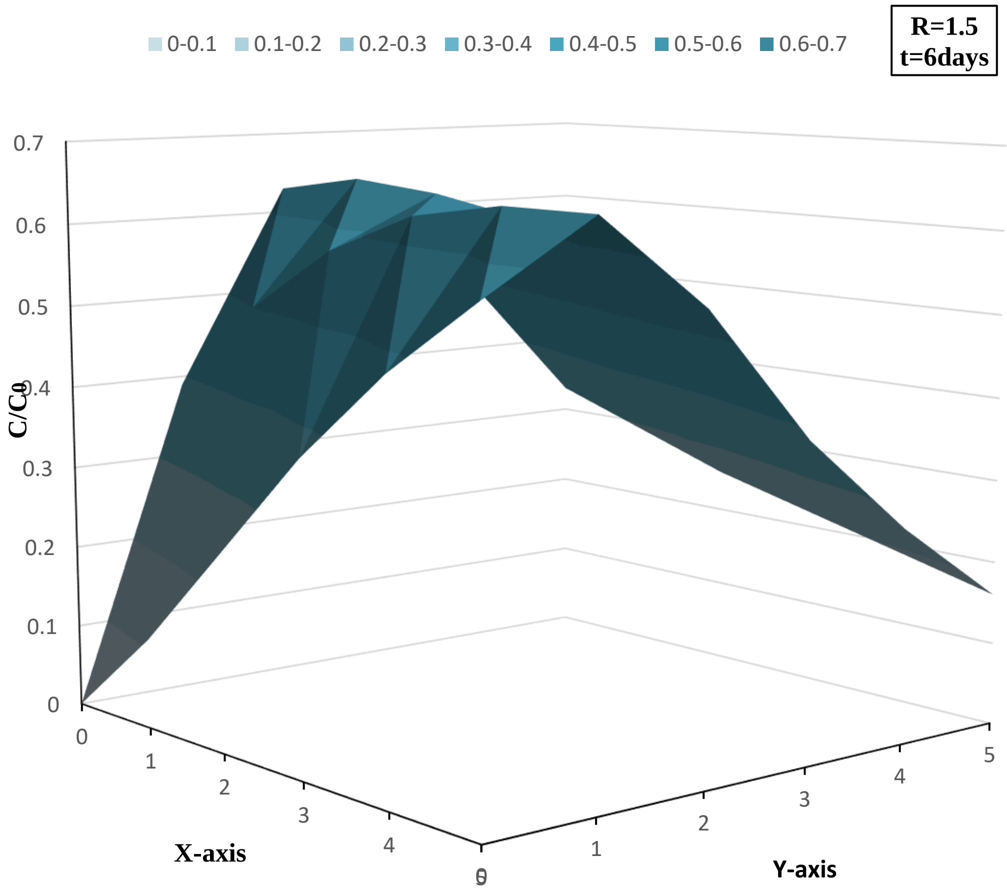


Figure.5 Concentration profiles of fluoride for steady flow for t=6 days(t>t_0) and R=1.5

Figure.5 and 6 are drawn at different time *t =6 days and t =12 days* and show that near the source boundary the concentration levels initially increases up to certain distance and then it deceases slowly with space.

But for higher value of *t* the maxima of concentration profiles are lower than that for lower value of *t*.

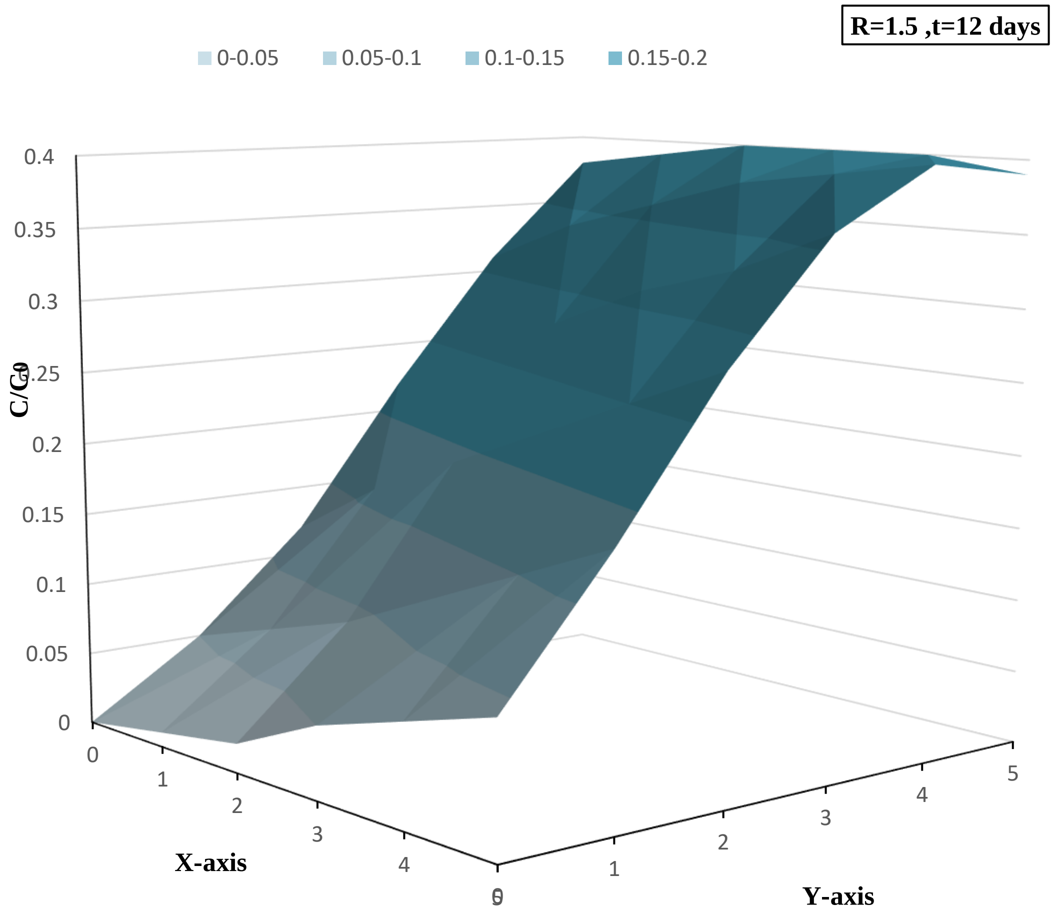


Figure.6 Concentration profiles of fluoride for steady flow for t=12 days ($t>t_0$) and R=1.5

On comparing the figure.7 with figure .5, it is observed that for high value of retardation factor, the concentration values are lower and vice-versa.

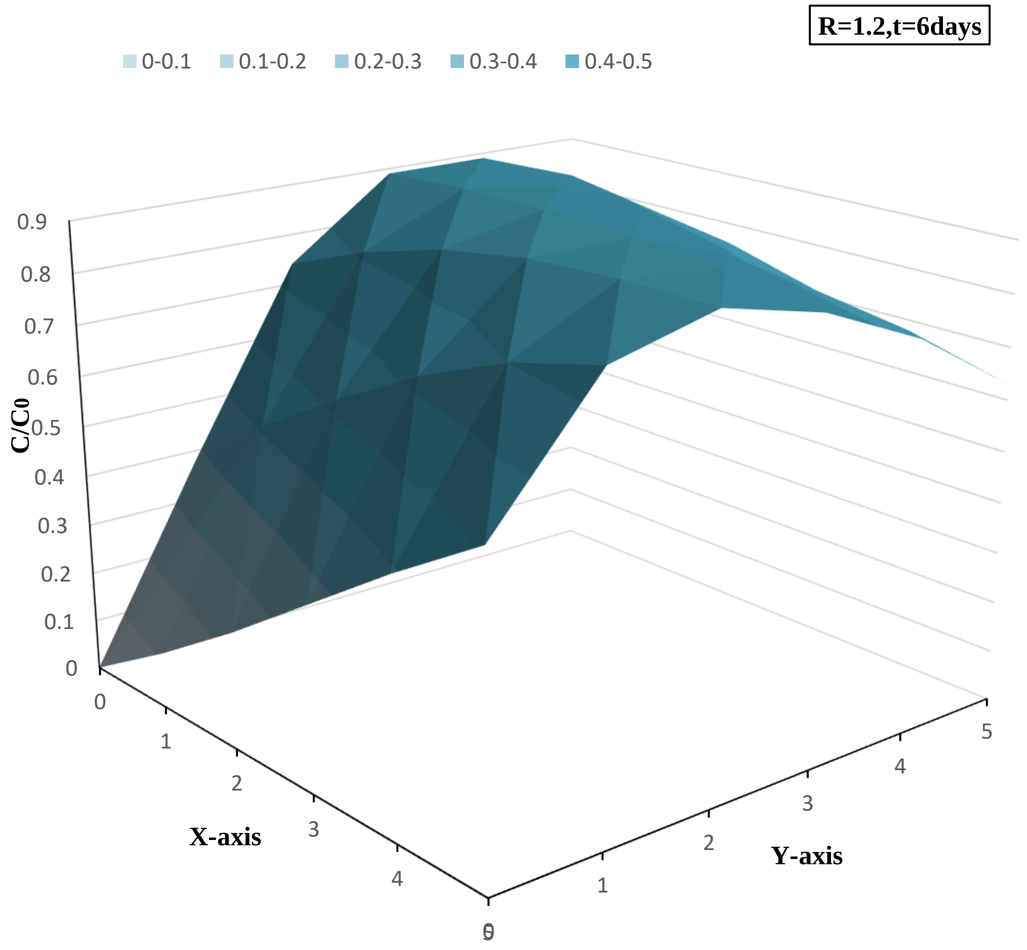
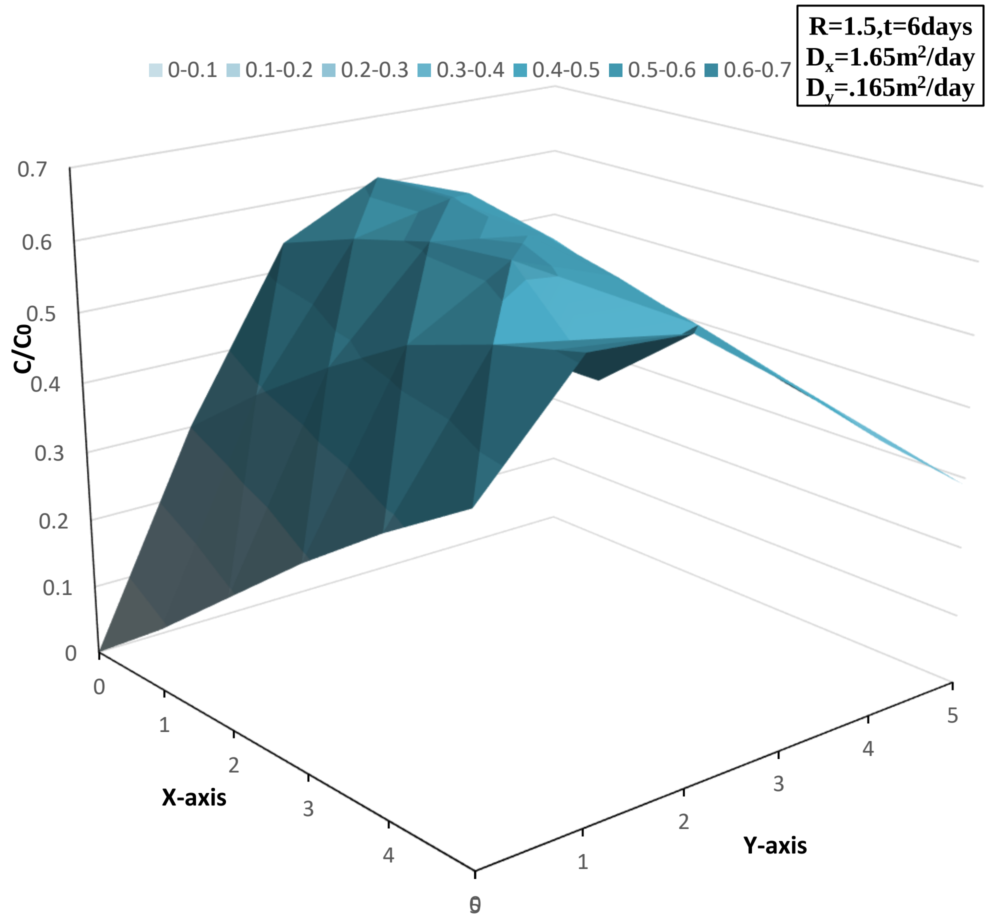


Figure.7 Concentration profiles of fluoride for steady flow for t=6 days ($t>t_0$) and R=1.2

Similarly, on comparing figure.8 with figure.5, it appears that near the source boundary the fluoride concentration levels initially increases for both and after some distance travelled it deceases but decreasing levels of concentration are lower for lower dispersion coefficient.



R=1.5,t=6days
D_x=1.65m^2/day
D_y=.165m^2/day

Figure.8 Concentration profiles of fluoride for steady flow for t=6 days (t >t_0) and R=1.5 for higher Dispersion coefficients

4.5 CONCLUSION

The present study presents a two-dimensional model for transport of fluoride ion in a homogeneous porous medium i.e. soil, in a steady state, considering both the longitudinal as well as transverse movement of the same. The equations so obtained have been solved analytically using Laplace transform technique. The numerical computation shows that the fluoride ion concentration decreases with respect to distance from origin along both longitudinal and transverse directions. There were often more influencing factors than initially anticipated, even in relatively simple systems. But on the whole, the transportation rules of fluorine ions are basically correct, which indicates that the established two-dimensional model can approximate the transportation rules of fluorine contaminants in homogeneous isotropic soils.

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Chapter 5

Modelling Assessment of Fluoride Transport with Transient Flow Conditions under the Influence of Chemical Moieties

5.1 INTRODUCTION

The problem of high fluoride concentrations in groundwater and risk of fluorosis associated with use of such fluorinated water for human consumption is faced by a large section of the world population. Fluoride, which is an important micronutrient required for human and animal health, may be highly toxic particularly if present in high concentrations. Most of the inorganic fluoride present in soil are either complexed with Al or Fe or remain in soluble ionic form in soil water. Sodium Fluoride (NaF) is the most important inorganic fluoride salt present in soil due to its high solubility in water.

The industries dealing with aluminium, steel, glass, and fertilizer are the main contributor to generation of fluoride wastes. When a great deal of fluoride pollutants is drained into the soil and the amount of pollutants exceeds the capacity of self-purification of the soil, pollutants will continue to leach downwards with water and pollute groundwater. Since Fluorine is reactive in nature, it infiltrates through the vadose zone [1] and reaches the water-table and continue to migrate in the direction of groundwater flow. Therefore, in order to avoid health risk, it is essential to understand the transport process of fluoride through the subsurface porous media. It is also crucial from the point of view of predicting and controlling the migration of fluoride in the soil-water system.

In recent years much more, attention has been focused on chemical transport in and through the vadose zone [2,3]as a result of increased use of agrochemicals such as fertilizers and pesticides and increased demands to store and dispose of industrial and municipal wastes such as sewage. The vadose zone is usually the first subsurface environment to encounter surface applied agrochemicals and contaminants and hence all surface and subsurface chemical concentrations and subsequent environmental impacts are inextricably linked to the physical, biological and chemical dynamics including sorption-desorption, volatilization, photolysis and degradation [4].

Richards' equation [5] coupled with the Fickian-based convection-dispersion equation for solute transport forms the major basis of any understanding of the physical and chemical processes in the vadose zone. Analytical and numerical solutions of these classical equations are widely used to study and predict water flow and solute transport for specific laboratory and field experiments and to extrapolate these results for other experiments in different soils, crops and climatic conditions.

Various mathematical models have been developed representing the transport of reactive contaminants through porous media over the years [6, 7, 8]. 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 [9, 10, 11].

The transport of chemicals, in presence of chemical moieties present in soil environment and groundwater, in porous media undergoes various chemical changes through advection, diffusion and dispersion. In addition, it involves other mechanisms like rate-limited sorption and desorption, biodegradation, and chemical reaction. 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 [12]. The solution of transport equation considered reversible and irreversible solute adsorptions. The irreversible adsorption was represented by the sink/source term.

The present study models the solute transport process of fluoride ion using the soil water column experiment [13], wherein the soil column is loaded with Sodium Fluoride (NaF) and the presence of OH^- ions is varied by diluting the extractant with Sodium Hydroxide (NaOH), Potassium Hydroxide (KOH) and Ammonium Hydroxide (NH_4OH). The experimental setup resembles the onsite conditions where presence of different salts in soil leads to change of pH of soil.

5.2 EXPERIMENTAL BACKGROUND

The experimental set up [13] is same as discussed in chapter 3. The leachate's pore volume was determined using equation (1) [14].

$$P_v = \frac{qt}{\theta V} \tag{1}$$

where

q =Volume of effluent collected per unit time i.e. flow rate $cm^3\ h^{-1}$

t =Time that has elapsed since the slug was introduced

θ =Water filled porosity cm^3/cm^3

V =Total volume of soil column.

In each experiment, a fixed volume of aqueous salt solution (slug) with desired anion concentration Sodium Fluoride (NaF) was added at the top of the soil column and was allowed to get adsorbed uniformly in the column for 24 hrs, after which the column was continuously leached with de-ionized water with Sodium Hydroxide (NaOH), Potassium Hydroxide (KOH) and Ammonium Hydroxide (NH_4OH) [13]. The flow rate of extractant measured was constant (2+0.5 ml/10 min). Till the soluble anions were completely removed, leaching was carried out. After which, the column soil was transferred into the beaker in a known volume of extractant and his salt solution was stirred for 2 hrs. The ion concentration was further determined in the filtrate of the soil suspension to ensure the complete removal of soluble ions from the soil in the column. The total leachable concentration was taken equal to the total leachable concentration present initially during leaching (i.e. concentration t=0). The concentration of ions was determined in leachate collected periodically at an interval of 2 min, during each kinetic run.

The undisturbed vertical soil column of the soil collected from Sambhar region of Rajasthan. [13] was loaded with Sodium Fluoride (NaF) and Sodium Hydroxide (NaOH), Potassium Hydroxide (KOH) and Ammonium Hydroxide (NH_4OH) were diluted with deionized water. The increase in fluoride leaching with increase in OH^- concentrations, as observed [13] is inevitable as the radii of Fluoride (F) and OH^- ions are comparable and an exchange of OH-F takes place. The cation attached to OH^- ion significantly affects fluoride, the maximum being with Ammonium Hydroxide (NH_4OH) and minimum with Potassium Hydroxide (KOH). The maximum leaching has been observed when Ammonium Hydroxide (NH_4OH) is added in percolating water because of H-F bonding with NH_4^+ can carry a greater number of F^- ions (at least 4) with single NH_4^+ ion.

5.3 THEORETICAL DEVELOPMENT AND GOVERNING EQUATIONS

In the present study the degradation pathway of the fluoride ion can be represented in a manner similar to [15], as

$$[C_i] \underset{\gamma_1}{\rightarrow} [C_{i+1}] \tag{2}$$

$$\downarrow \gamma_2$$

Here, γ_1 is the first order degradation constant for fluoride ion and γ_2 is the rate constant for hydrolysis.

In hydrolysis the chemical speciation of an organic contaminant gets changed. In this, as a result of the reaction of the fluoride salt with water, an exchange of some functional group from the salt with a hydroxyl (OH^-) group takes place. The extent of fluoride ion contamination attenuation by both bio degradation and hydrolysis depends on the chemical properties of the contaminant as well as the aqueous medium. The transformation processes in present case is shown to be following a first-order kinetic reaction [13].

The fluorides find their way into the soil subsurface predominantly by advection, that is by flow of groundwater, and by dispersion which is caused by mechanical mixing and molecular diffusion. Due to small seepage velocity molecular diffusion is neglected.

As the Sodium Fluoride (NaF) is introduced in to the soil system in the form of pulse i.e. for a time $t_0 > t$, the distance in downward direction i.e. longitudinal direction be represented by x [L]. In case of homogeneous porous formation, the dispersion coefficient, seepage velocity and rate constants for degradation and hydrolysis are functions of time only. Therefore, letting $D = D_0 f(t)$, $u = u_0 f(t)$, $\gamma_1 = \gamma^1 f(t)$ and $\gamma_2 = \gamma^2 f(t)$,the one-dimensional advection-diffusion equation is given as

$$R\frac{\partial C}{\partial t} = D_0 f(t)\frac{\partial^2 C}{\partial x^2} - u_0 f(t)\frac{\partial C}{\partial x} - (\gamma^1 + \gamma^2) f(t) C. \qquad (3)$$

Here $C = C(x, t)$ = concentration of fluoride at any time t; D_0 [LT^{-2}] =Uniform constant dispersion coefficient along x direction; u_0[LT^{-1}] = uniform constant velocity along x direction; R= retardation factor(dimensionless); γ^1 = uniform constant degradation constant; γ^2 = uniform constant hydrolysis constant.

The two forms of $f(t)$ are considered here, $f(t)=1-\sin mt$ and $f(t)=e^{-mt}$, where $mt<1$ and $m[T^{-1}]$is flow resistance coefficient.

The source of fluoride contamination is a uniform pulse-type point source that is, it is introduced into the porous medium continuously at a uniform rate up to a certain time period i.e. t_0 (24 hrs.) and for $t > t_0$ it becomes zero. The soil column is having some inherent initial concentration of fluoride C_i. Flux type homogeneous conditions are assumed at far ends of the medium, along both the directions. So, writing initial and boundary conditions mathematically

$$C(x,t) = C_i \;\; ; \quad x \geq 0\,, t = 0. \tag{4}$$

$$C(x,t) = \begin{cases} C_0\,; & 0 < t \leq t_0 \\ 0\;\;; & t \geq 0 \end{cases}, \tag{5a}$$

$$\frac{\partial C}{\partial x} = 0\,;\;\; ; x \to \infty, t \geq 0. \tag{5b}$$

5.4 ANALYTICAL SOLUTION

The problem of fluoride transport modelling in homogeneous porous medium can be solved using numerical, analytical, statistical, finite element method etc. It has been observed that the analytical approach is more significant to estimate the pattern of solute concentration and various transport parameters from field data [16,17]. Also, in the earlier chapter for one dimensional model, the analytical solution shows more comparison with observed experimental values.

A new time variable is introduced by the transformation [18]

$$T = \int_0^t f(t)dt, \tag{6}$$

$$\frac{\partial T}{\partial t} = f(t) \tag{6a}$$

Therefore,

$$\frac{\partial C}{\partial t} = \frac{\partial C}{\partial T}\frac{\partial T}{\partial t} = f(t)\frac{\partial C}{\partial T} \tag{7}$$

On substitution from equation (7) to equation (3), the obtained equation on simplification gives

$$R\frac{\partial C}{\partial T} = D_0\frac{\partial^2 C}{\partial x^2} - u_0\frac{\partial C}{\partial x} - (\gamma^1 + \gamma^2)C. \tag{8}$$

Now onwards and in succeeding equations writing $(\gamma^1 + \gamma^2) = \gamma$ and rewriting equation (8) after rearranging terms,

$$\frac{\partial C}{\partial T} = \frac{D_0}{R}\frac{\partial^2 C}{\partial x^2} - \frac{u_0}{R}\frac{\partial C}{\partial x} - \frac{\gamma}{R}C. \tag{9}$$

Now introducing the transformation

$$C(x,T) = K(x,T) exp\left[\frac{u_0 x}{2D_0} - \frac{1}{R}\left(\frac{{u_0}^2}{4D_0} + \gamma\right)T\right]. \tag{10}$$

The terms $\frac{\partial C}{\partial T}, \frac{\partial C}{\partial z}$ and $\frac{\partial^2 C}{\partial x^2}$ found from equation (10) to be used in equation (9) are as follows:

$$\frac{\partial C}{\partial T} = exp\left\{\frac{u_0 x}{2D_0} - \frac{1}{R}\left(\frac{{u_0}^2}{4D_0} + \gamma\right)T\right\}\left\{\frac{\partial K}{\partial t} - \frac{K}{R}\left(\frac{{u_0}^2}{4D_0} + \gamma\right)\right\}, \tag{11}$$

$$\frac{\partial C}{\partial x} = exp\left\{\frac{u_0 x}{2D_0} - \frac{1}{R}\left(\frac{{u_0}^2}{4D_0} + \gamma\right)T\right\}\left\{\frac{\partial K}{\partial x} + \frac{u_0 K}{2D_0}\right\}, \tag{12}$$

$$\frac{\partial^2 C}{\partial x^2} = exp\left\{\frac{u_0 x}{2D_0} - \frac{1}{R}\left(\frac{{u_0}^2}{4D_0} + \gamma\right)T\right\}\left\{\frac{\partial K}{\partial t} - \frac{K}{R}\left(\frac{{u_0}^2}{4D_0} + \gamma\right)\right\}. \tag{13}$$

Substituting the values from equation (11), (12) and (13) in equation (9) and simplifying the equation obtained is

$$R\frac{\partial K}{\partial T} = D_0\frac{\partial^2 K}{\partial x^2}. \tag{14}$$

As a result of the transformation used, given by equation (10), the initial condition and the boundary conditions given by equation (4) and (5a), (5b) respectively get transformed to

$$K(x,T) = C_i exp\left\{-\frac{u_0 x}{2D_0}\right\} \quad ; \quad x \geq 0, T = 0. \tag{15}$$

$$K(x,T) = \begin{cases} C_0 exp\left\{\frac{1}{R}\left(\frac{{u_0}^2}{4D_0} + \gamma\right)T\right\} ; \quad 0 < T \leq T_0 & , x = 0 \\ 0 \;\; ; \qquad T \geq 0 \end{cases} \tag{16a}$$

$$\frac{\partial K}{\partial x} + \frac{u_0 K}{2D_0} = 0 \; ; \; x \to \infty, T \geq 0 \tag{16b}$$

Applying the Laplace transform to equation (14), the expression obtained is

$$\frac{R}{D_0}[s\bar{K}(x,s) - K(x,0)] = \frac{d^2\bar{K}}{dx^2}. \tag{17}$$

From equation (15) putting value of *K (x, t)* at *t=0* in equation (17), the expression obtained is

$$\frac{d^2\bar{K}}{dx^2} - \frac{Rs}{D_0}\bar{K} = -\frac{R}{D_0}\left[C_i exp\left(-\frac{u_0 x}{2D_0}\right)\right]. \tag{18}$$

The complete general solution of equation (18) is obtained by sum of complementary function (C.F) and particular integral (P.I) as follows

$$C.F = C^1 \exp(n_1 x) + C^2 \exp(-n_2 x) \tag{19}$$

Where C^1 and C^2 are arbitrary constants to be found using initial and boundary conditions and n_1 and n_2 are the roots of the auxiliary equation $D'^2 - \frac{Rs}{D_0} = 0$ that is

$$n_1 = \sqrt{\frac{Rs}{D_0}} \; and \; n_2 = -\sqrt{\frac{Rs}{D_0}}.$$

And particular integral is

$$P.I=\frac{\left[C_i exp\left(-\frac{u_0 x}{2D_0}\right)\right]}{\left[s-\frac{u_0^2}{4RD_0}\right]} \tag{20}$$

So, the complete general solution of equation (18) is given as

$$\bar{K}(x,s)=C^1\exp\left(\sqrt{\frac{Rs}{D_0}}x\right)+C^2\exp\left(-\sqrt{\frac{Rs}{D_0}}x\right)+C_i\,\frac{exp\left(-\frac{u_0 x}{2D_0}\right)}{\left(s-\frac{{u_0}^2}{4RD_0}\right)}. \tag{21}$$

In order to find C^1 and C^2 ,finding Laplace transform of 16(a) using the Laplace transform definition $\bar{K}(x,s)=\int_0^\infty \mathrm{K(x,T)}\exp(-sT)dT$, where s= parameter, we have

$$\bar{K}(x,s)=\int_0^{t_0} C_0 exp\left\{\frac{1}{R}\left(\frac{{u_0}^2}{4D_0}+\gamma\right)T\right\}\exp(-sT)dT \tag{22}$$

$$\bar{K}(0,s)=\frac{C_0}{\left[s-\frac{1}{R}\left(\frac{{u_0}^2}{4D_0}+\gamma\right)\right]}\left[1-exp\left\{-\left(s-\{\frac{1}{R}\left(\frac{{u_0}^2}{4D_0}+\gamma\right)T_0\}\right)\right\}\right] \tag{23}$$

And Laplace transform of 16(b) is given as

$$\frac{d\bar{K}}{dx}+\frac{u_0\bar{K}}{2D_0}=0\,;\ x\rightarrow\infty, s\geq 0 \tag{24}$$

From equation (21)

$$\frac{d\bar{K}}{dx} = C^1\sqrt{\frac{Rs}{D_0}}\exp\left(\sqrt{\frac{Rs}{D_0}}x\right) - C^2\sqrt{\frac{Rs}{D_0}}\exp\left(-\sqrt{\frac{Rs}{D_0}}x\right) - \frac{u_0}{2D_0}C_i\,\frac{exp\left(-\frac{u_0x}{2D_0}\right)}{\left(s-\frac{{u_0}^2}{4RD_0}\right)} \tag{25}$$

Substituting above value of $\frac{d\bar{K}}{dx}$ in equation (24),

$$\frac{d\bar{K}}{dx} + \frac{u_0\bar{K}}{2D_0} = C^1\sqrt{\frac{Rs}{D_0}}\exp\left(\sqrt{\frac{Rs}{D_0}}x\right) - C^2\sqrt{\frac{Rs}{D_0}}\exp\left(-\sqrt{\frac{Rs}{D_0}}x\right) - \frac{u_0}{2D_0}C_i\,\frac{exp\left(-\frac{u_0x}{2D_0}\right)}{\left(s-\frac{{u_0}^2}{4RD_0}\right)} + \frac{u_0\bar{K}}{2D_0} = 0; \tag{26}$$

As $x \to \infty$

So, for above equation to be valid $C^1 = 0$. As a result equation (21) takes the form

$$\bar{K}(x,s) = C^2\exp\left(-\sqrt{\frac{Rs}{D_0}}x\right) + C_i\,\frac{exp\left(-\frac{u_0x}{2D_0}\right)}{\left(s-\frac{{u_0}^2}{4RD_0}\right)}. \tag{27}$$

Now, using condition (23) in equation (27) to find C^2

$$\bar{K}(0,s) = C^2 + C_i \frac{1}{\left(s - \frac{{u_0}^2}{4RD_0}\right)} = \frac{C_0}{\left[s - \frac{1}{R}\left(\frac{{u_0}^2}{4D_0} + \gamma\right)\right]}\left[1 - exp\left\{-\left(s - \{\frac{1}{R}\left(\frac{{u_0}^2}{4D_0} + \gamma\right)T_0\}\right)\right\}\right] \tag{28}$$

As a result,

$$C^2 = \frac{C_0}{\left[s - \frac{1}{R}\left(\frac{{u_0}^2}{4D_0} + \gamma\right)\right]}\left[1 - exp\left\{-\left(s - \{\frac{1}{R}\left(\frac{{u_0}^2}{4D_0} + \gamma\right)T_0\}\right)\right\}\right] - C_i \frac{1}{\left(s - \frac{{u_0}^2}{4RD_0}\right)} \tag{29}$$

So complete solution for equation (18) is,

$$\bar{K}(x,s) = \frac{C_0}{\left[s - \frac{1}{R}\left(\frac{{u_0}^2}{4D_0} + \gamma\right)\right]}\left[1 - exp\left\{-\left(s - \left\{\frac{1}{R}\left(\frac{{u_0}^2}{4D_0} + \gamma\right)T_0\right\}\right)\right\}\right]\exp\left(-\sqrt{\frac{Rs}{D_0}}x\right) - C_i \frac{1}{\left(s - \frac{{u_0}^2}{4RD_0}\right)}\exp\left(-\sqrt{\frac{Rs}{D_0}}x\right) + C_i \frac{exp\left(-\frac{u_0 x}{2D_0}\right)}{\left(s - \frac{{u_0}^2}{4RD_0}\right)} \tag{30}$$

Taking inverse Laplace transformation to equation (30) [19,20] and resubstituting for *K (x, T)*, we get

$$C(x,T) = C_0 F(x,T) + C_i F_1(x,T); \quad 0 < T \leq T_0, \tag{31a}$$

$$C(x,T) = C_0 F(x,T) - C_0 F(x,T - T_0) + C_i F_1(x,T); \quad T > T_0, \tag{31b}$$

Where

$$F(x,T) = \frac{1}{2} exp\left[\frac{\left(u_0 - \sqrt{{u_0}^2 + 4\gamma D_0}\right)x}{2D_0}\right] erfc\left[\frac{\left(Rx - \sqrt{{u_0}^2 + 4\gamma D_0}\,T\right)}{2\sqrt{RD_0T}}\right] + \frac{1}{2} exp\left[\frac{\left(u_0 + \sqrt{{u_0}^2 + 4\gamma D_0}\right)x}{2D_0}\right] erfc\left[\frac{\left(Rx + \sqrt{{u_0}^2 + 4\gamma D_0}\,T\right)}{2\sqrt{RD_0T}}\right], \tag{32a}$$

And

$$F_1(x,T) = \exp\left(-\frac{\gamma T}{R}\right)\left[1 - \frac{1}{2} erfc\left\{\frac{Rx - u_0T}{\sqrt{2D_0RT}}\right\} - \frac{1}{2} exp\left(\frac{u_0x}{D_0}\right) erfc\left\{\frac{Rx + u_0T}{\sqrt{2D_0RT}}\right\}\right] \tag{32b}$$

The procedure used to invert the Laplace transform [21]is to evaluate the closed contour and used the residue theorem. Branch point must be excluded from inside the contour and the original solution $C(x,T)$ can be obtained by finding the solution to

$$C(x,T) = \frac{1}{2\pi i}\int_{\tau+i\infty}^{\tau-i\infty} \bar{K}(x,s)\exp(sT)\,dT \tag{33}$$

$$C(x,T) = \sum_i Res(i) + \frac{1}{2\pi i}\oint \bar{K}(x,s)\exp(sT)\,dT \tag{34}$$

where *Res (i)* are the residues at the poles of $\bar{K}(x,s)$ which lie to the left of the line τ and outside of the contour Ω.

Poles of the expressions are $s = \frac{1}{R}\left(\frac{{u_0}^2}{4D_0} + \gamma\right); s = \frac{{u_0}^2}{4RD_0}$ and residue at them is obtained

$$Res\ at\left(s=\frac{1}{R}\left(\frac{{u_0}^2}{4D_0}+\gamma\right)\right)=\lim_{s\to\frac{1}{R}\left(\frac{{u_0}^2}{4D_0}+\gamma\right)}\left(s-\frac{1}{R}\left(\frac{{u_0}^2}{4D_0}+\gamma\right)\right)f(s)\exp(sT) \tag{35}$$

$$Res\ at\left(s=\frac{{u_0}^2}{4RD_0}\right)=\lim_{s\to\frac{{u_0}^2}{4RD_0}}\left(s-\frac{{u_0}^2}{4RD_0}\right)f(s)\exp(sT) \tag{36}$$

On summing up the residues the resultant solution for $C(x,T)$ so obtained is given by equation (31a) and (31b).

5.5 RESULTS AND DISCUSSION

This section shows the results obtained numerically in the form of initial leaching rate profile for $[F^-]$ ion leaching for added salt Sodium fluoride (NaF) in presence of OH^- ions, which is varied by diluting the extractant with Sodium Hydroxide (NaOH), Potassium Hydroxide (KOH) and Ammonium Hydroxide (NH_4OH).

The specified values of parameters are taken as [13] *pH=10.5; R=Retardation factor =15; x=L=column length=60cm;* $P_e = 2$ k^1 *=0.00414/sec;* k_1'*= 0.001/sec* NH_4OH*;* k_1'*= 0.0005/sec for NaOH and* k_1'*= 0.00025/sec for KOH as per the observed experimental results; flow rate of extractant =2.5ml/10min and m=0.1/sec.*

The leaching profiles in Figure.1,2 and 3 represent the plotted graph between time and the $[F^-]_l$ that is leachable fluoride remaining at time t in the soil column in presence of different extractant with Sodium Hydroxide (NaOH), Potassium Hydroxide (KOH) and Ammonium Hydroxide (NH_4OH) respectively for the values of $[F^-]_{ad}$*=166mg/kg* .In the laboratory experiment by Saxena and Rani (2012) the fluoride source is supplied for predefined time t_0(24 hrs) that is it has a finite pulse source and the flow rate and dispersion are constant therefore *m=0* .The leaching profiles in Figure

4,5 and 6 represent the plotted graph between time and the $[F^{-}]_{l}$ that is leachable fluoride remaining at time t in the soil column for *m=0.1/sec* considering *f(t)=e*$^{-mt}$ *and f(t)=1-sinmt.*

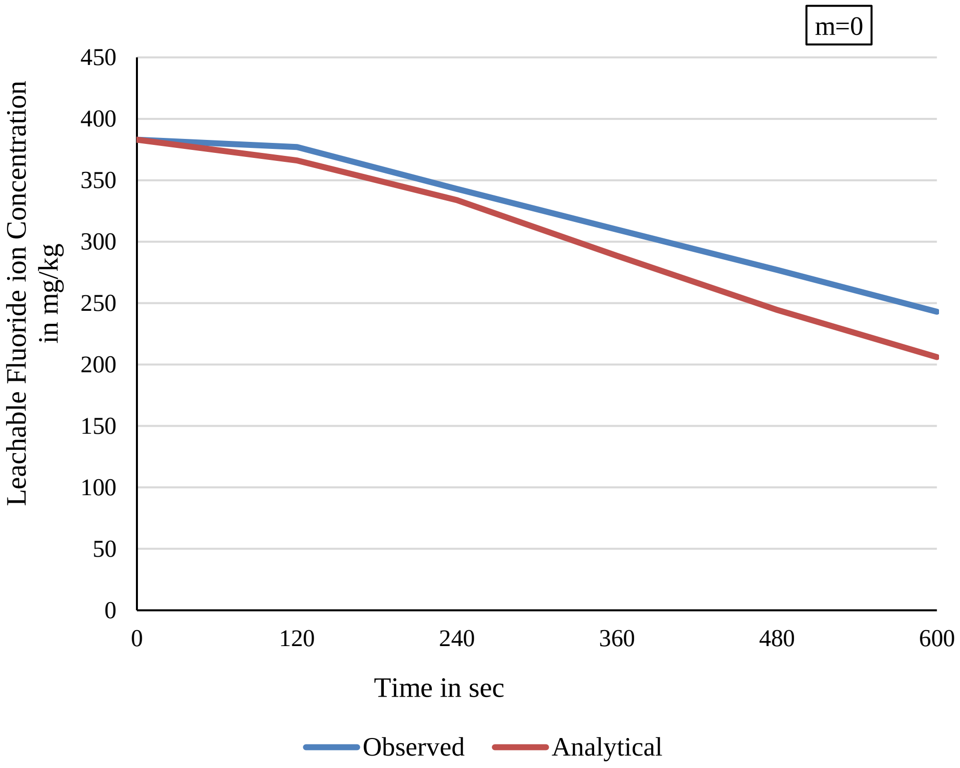

Fig.1 Leachable Fluoride ion concentration vs time when $[F^{-}]_{ad}$ =166 mg/kg and extractant is NH4OH.

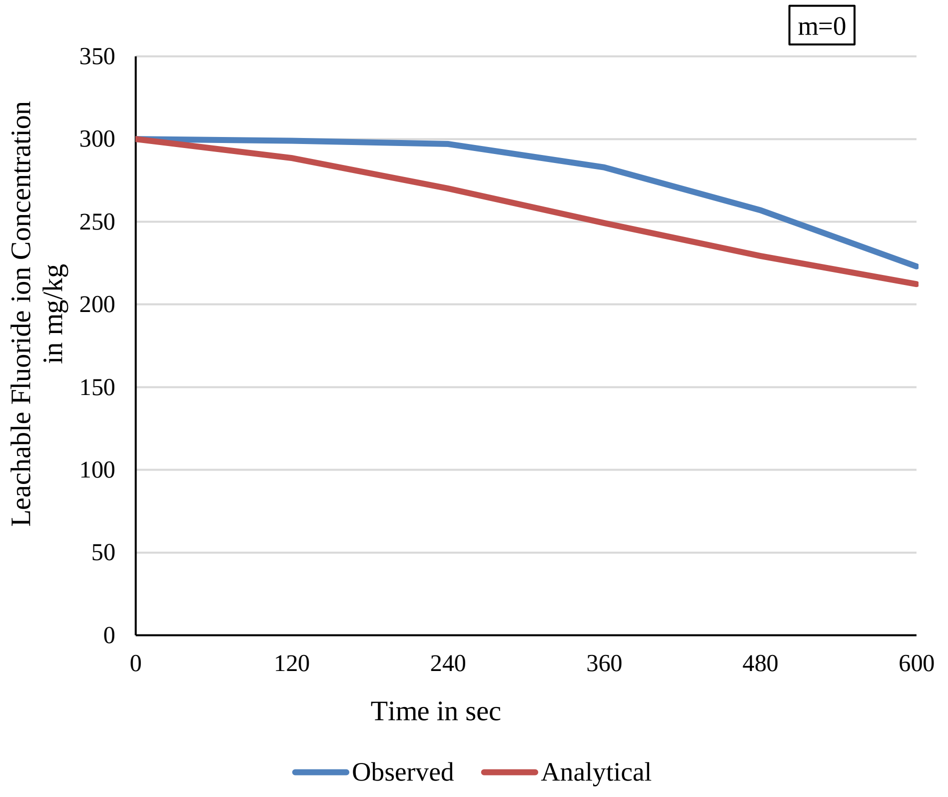

Fig.2 Leachable Fluoride ion concentration vs time when $[F^{-}]_{ad}$ =166 mg/kg and extractant is NaOH.

From the figures 1,2 and 3 it is clear that increased fluoride leaching takes place with increase in OH- concentrations as the radii of F^- and OH^- ions are comparable and an exchange of F^- and OH^- ions is inevitable. The cation attached to OH^- ion which affected F^- leaching significantly, the maximum being with Ammonium Hydroxide (NH_4OH) and minimum with Potassium Hydroxide (KOH). Ammonium NH_4^+ ions which can carry at least 4 F^- ion through H-F bond [22] result in highest leaching as a result the leachable fluoride concentration is more in the order of KOH>NaOH>NH_4OH.

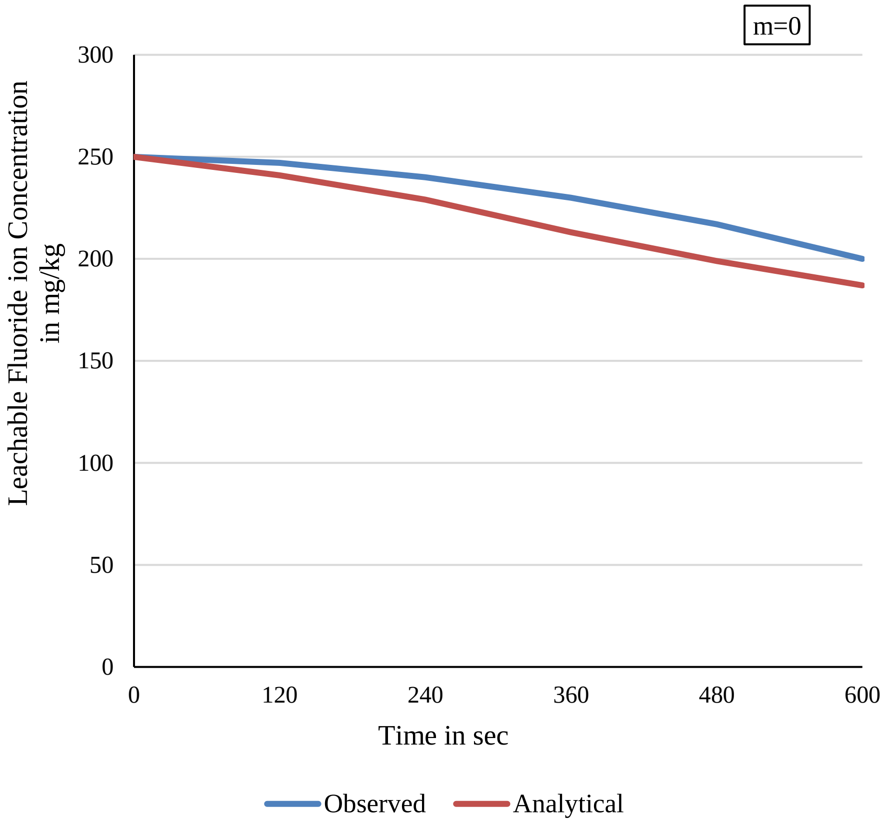

Fig.3 Leachable Fluoride ion concentration vs time when $[F^{-}]_{ad}$ =166 mg/kg and extractant is KOH.

The maximum leaching occurs on adding NH4OH and minimum with KOH. The analytical solutions offer good comparison with the observed results for soil column experiment [13].

The soil column experiment is based on steady state assuming the flow velocity to be constant throughout the experiment. Figures 4, 5 and 6 show the analytical results under transient flow conditions, by taking $f(t)=e^{-mt}$ *and* $f(t)=1-\sin mt$.

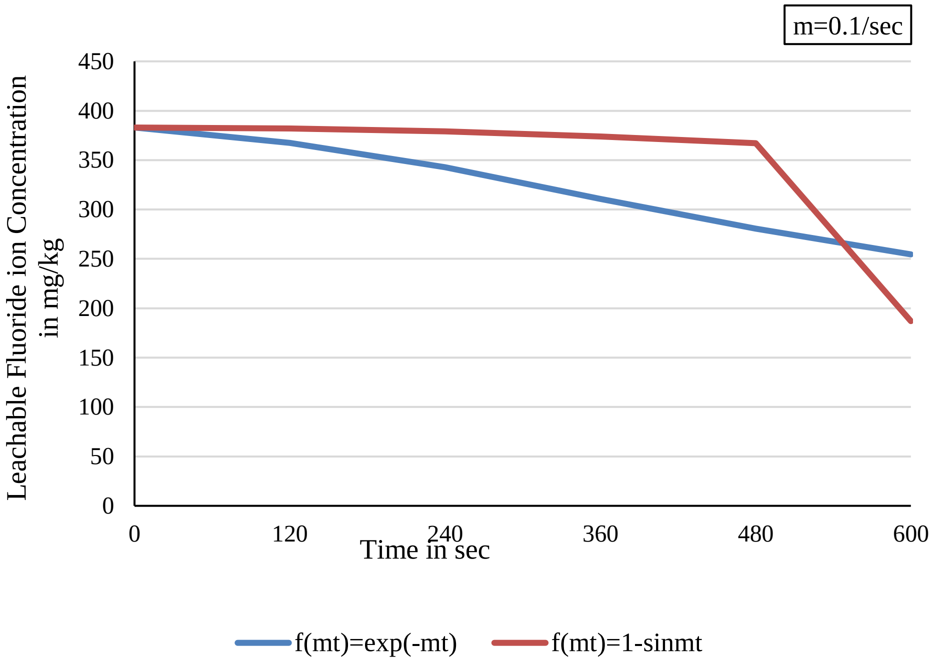

Fig.4 Leachable Fluoride ion concentration vs time when $[F^-]_{ad}$ =166 mg/kg and extractant is NH4OH.

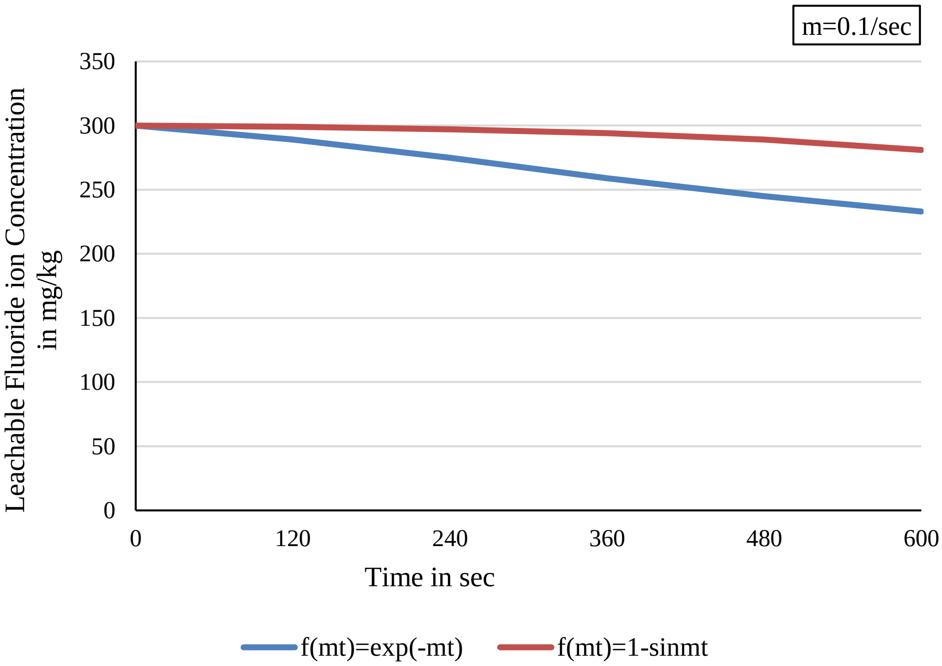

Fig.5 Leachable Fluoride ion concentration vs time when $[F^-]_{ad}$ =166 mg/kg and extractant is NaOH.

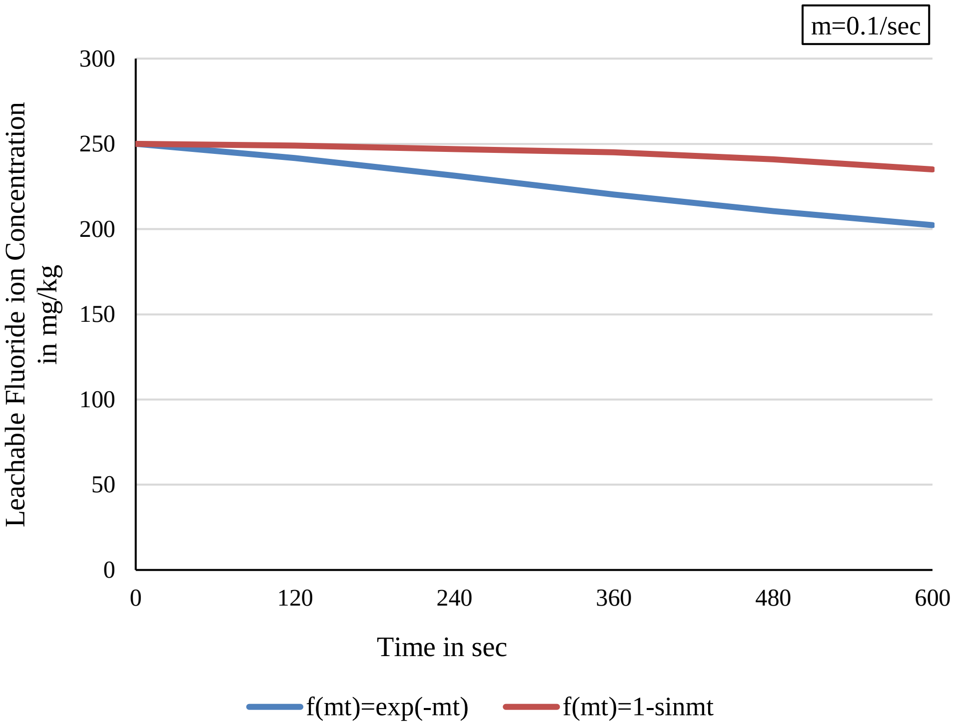

Fig.6 Leachable Fluoride ion concentration vs time when $[F^{-}]_{ad}$ =166 mg/kg and extractant is KOH.

The above plots in figure 4,5 and 6 show that under transient flow conditions, for the exponential form of velocity, the leachable fluoride ion concentration decreases faster than in the sinusoidal form of velocity. The concentration levels for sinusoidal form of velocity are higher than that of exponential form of velocity.

5.6 CONCLUSION

The present study presents an analytical solution to solve the one-dimensional advection–dispersion equation for describing the behaviour and transport of fluoride ion in a homogeneous porous media in presence of different chemical moieties present in soil environment and groundwater. The different extractants, whose impact on fluoride transport in soil was studied analytically were Sodium Hydroxide (NaOH), Potassium Hydroxide (KOH) and Ammonium Hydroxide (NH_4OH). In the derived solution, along with steady state conditions as used in soil column experiment in laboratory [13], the velocity has been assumed to be both exponentially deceasing function of time as well as sinusoidal. The analytical results obtained for uniform constant flow velocity show a good comparison with experimentally observed values of fluoride ion concertation. The governing solute transport equation is solved analytically by employing Laplace Transformation Technique (LTT). The derived solution is an effective and useful one for further application to field studies, where the hydrological properties of the medium and prevailing boundary and initial conditions are the same as, or can be approximated by, the ones considered in this study.

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Chapter 6

Modeling Chemical ion Transport with Laplace Adomian Decomposition Method

6.1 INTRODUCTION

It is not an overstatement that most physical phenomena are modelled and described by partial differential equations and most of these phenomena are non-linear by nature. The fluid -flow in soil is modelled with the help of partial differential equations and non-linearity is a recurrent problem in modelling soil science problems. The equations governing fluid flow in soil involves nonlinear partial differential equations. A numerical Laplace decomposition algorithm to solve a class of nonlinear differential equations was proposed [1] and this method was applied this method for the solution of Duffing equation [2]. This method was used to solve Falkner-Skan equation [3]. The efficacy of Laplace Transform to solve the nonlinear differential equations by utilizing the decomposition technique is being outlined by numerical system.

It has been observed that application of a combination of Laplace transform method and Adomian decomposition method namely Laplace Adomian decomposition method (LADM) to solve a certain class of problems is very useful. The equivalence of the Adomian decomposition method for a system of linear Volterra integral equations and the successive approximations method, so called Picard's method, have also been studied [4]. The Laplace Adomian decomposition method has been used to solve a system of ordinary differential equations [5]. The method has been applied to solve non-linear Volterra integro-differential equations [6] and a system of ordinary differential equations [7]. Local fractional Laplace decomposition method has been discussed for numerical solutions of telegraph and Laplace equations on cantor sets [8]. Adomian Decomposition method has been used for solution of fuzzy heat equations also [9].

In the present paper, the effect of an external pressure / force in the form of gravitational force on flow through a porous medium has been studied by assuming the flow to be Newtonian. The flow of a viscous fluid through a porous medium bounded by a vertical surface [10] and application of Brinkman model in viscous incompressible flow through a porous channel has been studied [11]. The present study is carried out by employing Laplace Adomian Decomposition Method [12, 13 ,14] and some important predictions can be made on the basis of the present study. The rapidly converging analytical approximate solution of nonlinear ordinary or partial differential equation is given by decomposition method [13,14]. The choice of operator determines the speed of convergence. The operator may be a highest-ordered differential operator or a combination of linear operators or a multidimensional operator. To handle the nonlinear terms, the method does not take the help of any simplification. The use of decomposition parameter is made only to group the terms. Thus, the non-linearities can be handled easily in the operator equation and accurate approximate solution may be obtained for any physical problem. The study has been carried out for the flow in soil subject to external forces like gravity.

6.2 MATHEMATICAL MODELING OF THE PROBLEM

Nomenclature: (x, y) : Cartesian coordinates of a point, (u, v): Velocity components along x- and y- directions, U_0: Characteristic velocity, F_0: Applied external force, k: Permeability of porous matrix, h: Half-width of channel, η: Non-dimensional distance, μ: Coefficient of viscosity, v: Kinematic viscosity of solute, ρ: Density of solute, R_e: Reynolds number.

A transport system mainly consists of three-dimensional (3D) vessels. However, in some cases, such as in micro-vessels of soil it can be approximated to a two-dimensional (2D) and can be considered as a channel flow. A physical sketch of the geometry is shown in Figure 1. The x-axis is taken along the centre line of the channel, parallel to the channel surface and *y*-axis in the transverse direction. The flow is taken to be symmetric about *x*-axis [15].

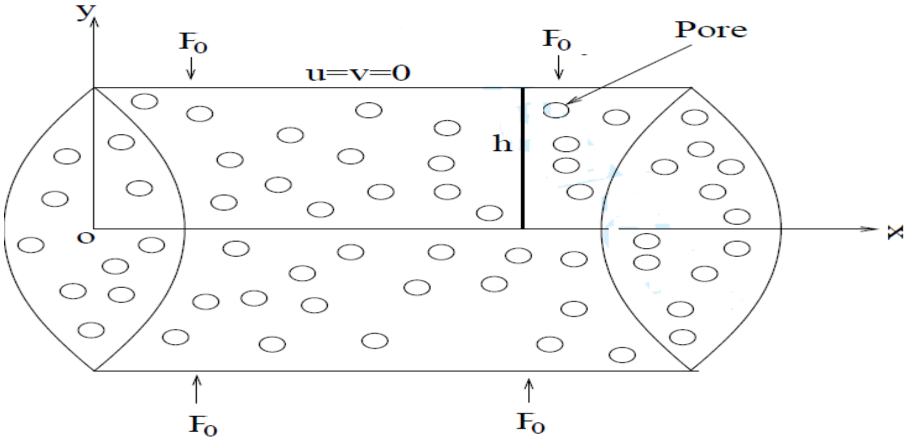

Figure 1: Physical Sketch of the Problem

However, the solutions of multidimensional transient flow of any solute can be obtained by numerical modelling, their applications are limited in the field. From a hydrological perspective, the solute movement in soil and its spatial distribution can largely be controlled by the water fluxes of the groundwater. For an improved understanding of the magnitude of these fluxes, accurate estimates of the temporal and spatial water uptake patterns are needed.

Let u and v be the velocity components along *x*- axis and *y*-axis respectively and F_0 be the applied external pressure. The equation for boundary layer flow of an incompressible fluid in the absence of pressure gradient,

$$u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}=\upsilon\frac{\partial^2 u}{\partial y^2}-\frac{\upsilon}{k}u-\frac{F_0^2 u}{\rho}, \qquad (1)$$

and the continuity equation is

$$\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}=0, \tag{2}$$

where, ρ is the density of solute, υ is the kinetic coefficient of viscosity and k denotes the permeability of the porous medium. Assuming that the flow is symmetric about the central line $y=0$ of the channel, we focus our attention to the flow in the region $0 \le y \le h$only. Then the boundary conditions to be taken care of are as follows:

$$u=v=0 \qquad at \quad y=h, \tag{3}$$

and

$$\frac{\partial u}{\partial y}=0, v=0 \quad at \ y=0. \tag{4}$$

We now introduce the non-dimensional quantities defined by

$$\zeta=\frac{x}{h}\ , \qquad \eta=\frac{y}{h}\ , \qquad u=\frac{U_0}{h}f'(\eta), \qquad v=-U_0\, f(\eta), \tag{5}$$

where U_0 is the characteristic velocity.

It may be noted that the continuity equation (2) is automatically satisfied.

In terms of the non-dimensional variables, Equation (1) reads

$$f'''+R_e(ff''-f'^2)-f'H=0. \tag{6}$$

Where R_e and K are the Reynolds number and porosity permeability parameter respectively, defined by

$$R_e=\frac{U_0 h}{\nu}, K=\frac{k}{h^2}\ , H=\left[F_0^2+\frac{1}{K}\right]. \tag{7}$$

With the use of transformation (5), the boundary conditions (3) and (4) become

$$f'=f=0 \quad at \ \eta=1, \tag{8}$$

and

$$f = f'' = 0 \quad at \;\; \eta = 0. \tag{9}$$

The equation (6) reduces to

$$f''' - f'H = 0,$$

when Reynolds number R_e is zero and have solution of the form

$$f = C_1 + C_2 e^{a\eta} + C_3 e^{-a\eta},$$

where $a = \sqrt{H}$.

At $\eta = 0\,, f = 0\,, f'' = 0$, gives $C_1 + C_2 + C_3 = 0$ and $a^2C_2 + a^2C_3 = 0$.

implying

$$f = 2C_2 sinha\eta,$$

and
$$f' = 2aC_2 cosha\eta.$$

If $\eta = 0$ and $f'(0) = b$

$$f = \frac{b}{a} sinha\eta. \tag{10}$$

6.3 ANALYSIS OF THE MODEL

In this section the model is analysed by solving equation (6) subject to the boundary conditions (8) and (9). For this purpose, the Laplace Adomian Decomposition Method (LADM) [16,17] is used. Taking the Laplace transformation of equation (6), we get

$$L[f'''] + R_e L[ff'' - f'^2] + HL[f'] = 0, \tag{11}$$

Here and in the sequel, L[F] stands for the Laplace transform of the function F.

Using the property of the Laplace transform, we have

$$\begin{gathered} s^3L[f]-s^2f(0)-sf'(0)+R_eL[ff'-f'^2] \\ -H[sL[f]-f(0)]=0 \end{gathered} \tag{12}$$

Using the boundary condition (9), in equation (12) we obtain

$$s(s^2-H)L[f]=-R_eL[ff''-f'^2]+sf'(0), \tag{13}$$

Writing $f'(0)=b$ (where b is a constant), equation (13) takes the form

$$L[f]=\frac{b}{s^2-H}-\frac{R_e}{s(s^2-H)}L[ff''-f'^2]. \tag{14}$$

Following Adomian Decomposition Method, we assume the solution for f in the form of an infinite series:

$$f=\sum_{n=0}^{\infty}f_n, \tag{15}$$

To write it in the form

$$\phi(\eta)=ff''-f'^2 \;\; ; \;\; \phi(\eta)=\sum_{n=0}^{\infty}A_n, \tag{16}$$

where $A_n=A_n(f_0,f_{1,\ldots\ldots,}f_n)$, are the so-called Adomian polynomials [12]. To find A_n, we introduce a scalar λ such that

$$f(\lambda)=\sum_{n=0}^{\infty}\lambda^n f_n, \tag{17}$$

The parameter λ ,used in (17) is used only for grouping the terms of different orders and not a perturbation parameter. Thus, the parameterized form of (16) is given by

$$\phi(\lambda)=\sum_{n=0}^{\infty}\lambda^n\left(\sum_{i=0}^{\infty}f_if''_{n-i}-\sum_{i=0}^{\infty}f'_if'_{n-i}\right). \tag{18}$$

From the definition of Adomian polynomials, it follows that

$$A_n = \frac{1}{n!}\frac{d^n}{d\lambda^n}(\phi(\lambda))_{\lambda=0}. \tag{19}$$

Now substituting (18) into (19), we get

$$\begin{gathered}
A_0 = f_0' f_0 - f_0'^2, \\
A_1 = f_0 f_1'' + f_1 f_0'' - 2 f_0' f_1', \\
A_2 = f_0'' f_2 + f_1'' f_1 + 2 f_0' f_2'' - f_1'^2, \\
A_3 = f_0'' f_3 + f_1'' f_2 + f_2'' f_1 - f_3' f_0 - 2 f_0' f_3' - 2 f_1' f_2' \,,
\end{gathered} \tag{20}$$

and so on. Substitution of equations (15) and (16) into the equation (14), further yields

$$L\left[\sum_{n=0}^{\infty} f_n\right] = \frac{b}{s^2 - H} - \frac{R_e}{s(s^2 - H)} L\left[\sum_{n=0}^{\infty} A_n\right]. \tag{21}$$

Matching both sides of equation (21) yields the iterative algorithm:

$$L[f_0] = \frac{b}{s^2 - H} \quad , \tag{22}$$

$$L[f_1] = -\frac{R_e}{s(s^2 - H)} L[A_0], \tag{23}$$

$$L[f_2] = \frac{R_e}{s(s^2 - H)} L[A_1], \tag{24}$$

$$L[f_3] = \tfrac{R_e}{s(s^2 - H)} L[A_2], \tag{25}$$

and so on. Now considering the inverse Laplace transform of equation (22) the following value of f*0* is obtained for $a = \sqrt{H}$:

$$f_0 = \frac{b}{a} \sinh(a\eta) \,. \tag{26}$$

The first Adomian polynomial A_0 calculated from eqns. (20) and (26) is found in the form

$$A_0 = -b^2. \tag{27}$$

Since $L[A_0] = [-b^2] = -\frac{b^2}{s}$; by applying Laplace inversion, we obtain

$$f_1 = \frac{b^2 R_e}{a^2}\left(\frac{1}{a}\sinh(a\eta) - \eta\right). \tag{28}$$

Proceeding in a similar manner, using (20) and (28), we calculate the second Adomian polynomial A_1 given by

$$A_1 = -\frac{2b^2 R_e}{a^2} - \frac{b^3 R_e}{a}\eta\sinh(a\eta) + \frac{2b^3 R_e}{a^2}\cosh(a\eta). \tag{29}$$

Next, we find the Laplace transformation of A_1 given by (29), substitute it in (24) and then consider Laplace inversion. Thus, we have found the expression of f_2 given below.

$$\begin{aligned} f_2 = \frac{2b^3 R_e}{a^2}\Bigg[\frac{1}{a^2}\Bigg(&\frac{1}{a}\sinh(a\eta) - \eta - \frac{1}{2a^2}(\eta\cosh(a\eta) \\ &- \frac{\sinh(a\eta)}{a} + \frac{1}{8}(\eta^2\sinh(a\eta) - \frac{3}{a}(\eta\cosh(a\eta) \\ &- \frac{\sinh(a\eta)}{\eta})\Bigg)\Bigg], \end{aligned} \tag{30}$$

If we consider three-term approximation of the solution

$$f = f_0 - f_1 - f_2, \tag{31}$$

By taking $\lambda = 1$; the calculated expression for f reads

$$f(\eta) = \frac{b}{a}\sinh(a\eta) + \frac{b^2 R_e}{a^2}\left(\frac{\sinh(a\eta)}{a} - \eta\right) \tag{32}$$

$$+ \frac{2b^3 R_e^2}{a^2}\left(\frac{1}{a^2}\left(\frac{3}{2a}\sinh(a\eta) - \eta - \frac{1}{2}\cosh(a\eta)\right)\right.$$

$$\left. + \frac{1}{8}\left(\eta^2 \sinh(a\eta) - \frac{3}{a}\left(\eta\cosh(a\eta) - \frac{\sinh(a\eta)}{a}\right)\right)\right).$$

The results coincide with equation (10) when Reynolds number is zero. The first derivative of $f(\eta)$ is given by

$$f'(\eta) = b cosh(a\eta) + \frac{b^2 R_e}{a^2}(\cosh(a\eta) - 1) \tag{33}$$

$$+ \frac{2b^2 R_e^2}{a^2}\left(\left(\frac{3}{a}\eta\cosh(a\eta) - \frac{\sinh(a\eta)}{a} - 1\right)\right.$$

$$\left. + \frac{a^2}{8}(\eta^2 \operatorname{acosh}(a\eta) - \eta\sinh(a\eta))\right).$$

Now using the boundary condition $f_1'(1) = 0$, we can obtain the expression for b in the form

=

$$\frac{-(cosha - 1) + \sqrt{4sinh^4 a + a\left(2 + \frac{a}{2}\right) + sinha + (a^3 - 8)cosh2a - 12cosh^2 a}}{4\frac{R_e}{a^2}\left(\frac{3}{2}cosa - \frac{a}{2}sina - 1 + \frac{a^3}{8}cosa - \frac{a^2}{8}sina\right)} \tag{34}$$

The volumetric flow rate is then given by

$$V_m = 2\int_0^1 f'(\eta)d\eta\,, \tag{35}$$

$$= 2\left[\frac{bsinha}{a} + \frac{b^2}{a^2}R_e\left(\frac{sinha}{a} - 1\right) + \frac{b^3R_e}{a^4}\left(\frac{3sinha}{a} - cosha - \frac{3}{2}\right) + \frac{a^2}{2}\left(\left(1 + \frac{3}{a^2}\right)sinha - \frac{3}{a}cosha\right)\right]. \quad (36)$$

$f''(1)$ can be obtained by differentiating equation (33) and then considering $\eta = 1$.

6.4 RESULTS AND DISCUSSION

The important results from present study are presented here in terms of pertinent dimensionless parameters. However, for practical considerations, we also mention some typical values of the corresponding dimensional parameters, as appropriate to the results subsequently obtained.

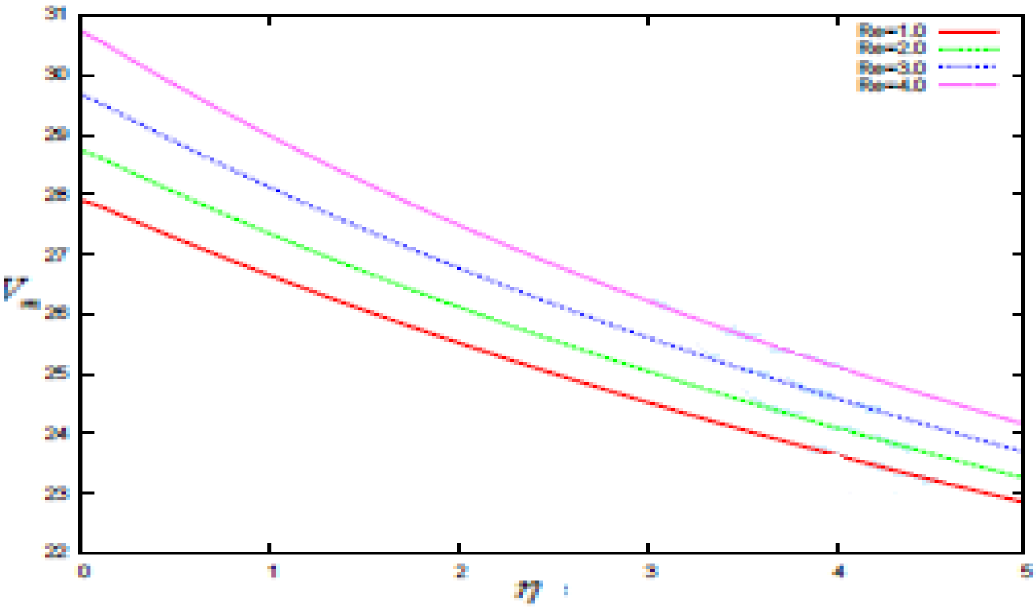

Figure. 2: Distribution of V_m with η different values of Reynolds number R_e

In finding the estimates, we have taken density, $\rho = 1440 kg.m^{-3}$, viscosity of the solute $\mu = 10^{-3} kg.m^{-1}s^{-1}$. Figure 2 illustrates the extent of variation in the volumetric flow rate corresponding to different values of Reynolds number R_e= 1.0, 2.0, 3.0, 4.0. The plots presented in this figure reveal that volumetric flow rate increases with a rise in the value of the Reynolds *Re.* The variation of f' and f with η are shown in Figure 3 and Figure 4 respectively.

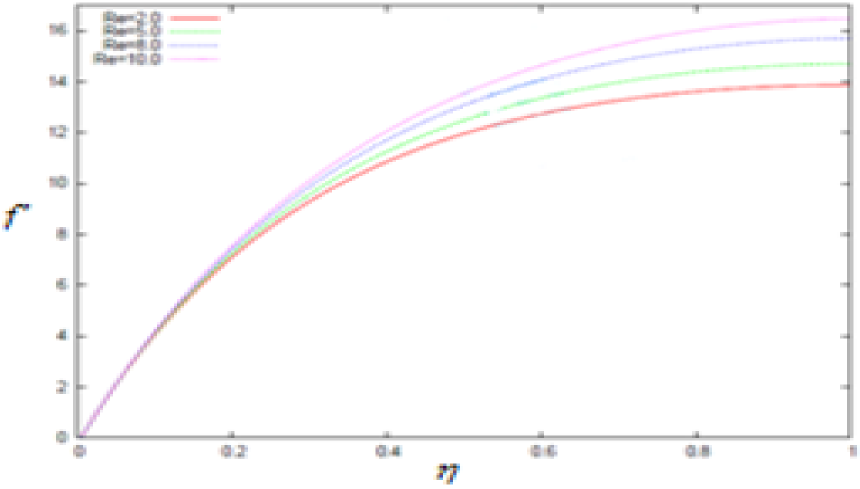

Figure 3: Distribution of f' with η for different values of Reynolds number R_e

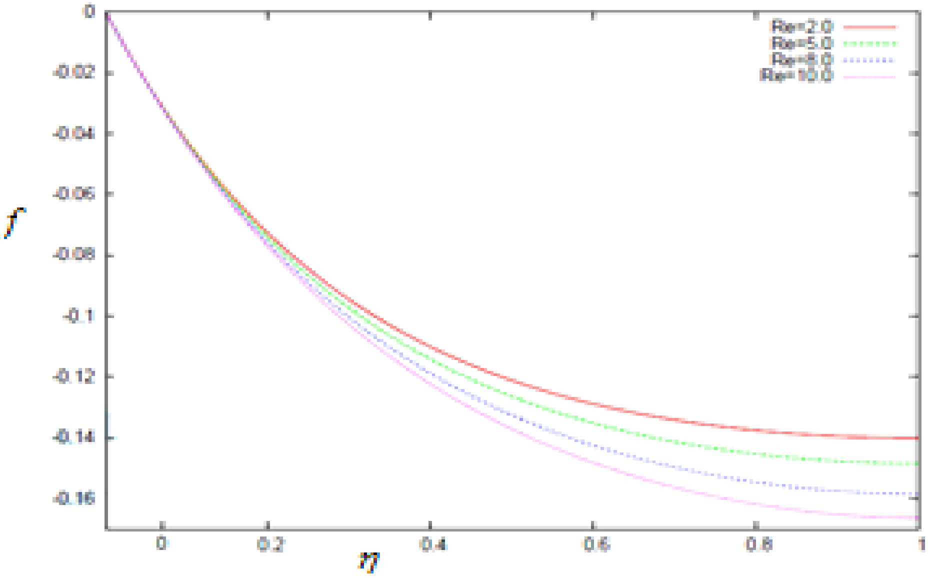

Figure 4: Distribution of f *with* η for different values of Reynolds number R_e

6.5 CONCLUDING REMARKS

The numerical results estimated are presented graphically in Figures 2-4. These figures illustrate the variation of the axial and transverse velocities in the channel flow of solute with change in Reynolds number R_e.

The present study deals with a theoretical investigation of solute flow through a porous soil under the action of an external force. The study is quite suitable for the application to the hydro-dynamical flow when it is subjected to the influence of an externally applied force. The solution to the nonlinear equations that govern the flow is obtained by using Adomian's decomposition method which is a powerful and efficient technique to get analytical approximate solution of nonlinear ordinary or partial differential equations and is rapidly convergent [13,14].

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Chapter 7

Future Scope and Prospects

7.1 PRESENT STUDY:

Fluoride, mainly found as sodium fluoride or hydrogen fluoride which are present in minerals fluorspar, fluorapatite, topaz and cryolite, is the 13th most abundant element of the earth crust and represents about 0.3 g/kg of earth's crust. The slow increase of fluoride concentrations in topsoil and as a result groundwater is caused by the fluoride content of soils which is inherited from parent material through atmospheric pollution and phosphatise fertilizers including industrial deposit.

Fluoride, if taken in different concentrations, is a vital substance for humans in preventing cavity and in facilitating the mineralization of arduous tissues. However, the excessive levels of fluoride in the groundwater pose major public health challenges in many regions of the world [1]. The limit varies among countries and therefore the age of individuals exposed. World Health Organization (WHO) has set a limit between 0.5 and 1.0 mg/L [2].

As per literature available on India, fluoride was first detected in Nellore district of Andhra Pradesh in 1937. More than one lakh villages, with more than 10 million people, stand to face disability and other serious health problems because of high Fluoride in their water across 22 States and more than 200 districts of India [3]. Rajasthan has the maximum number of Fluoride affected areas between 1 ppm-3 ppm, 3 ppm to 5 ppm and greater than 5 ppm [3].

The present study presents a mathematical approach for transport of fluoride ion in soil so as to facilitate the assessment and prediction of fluoride in soil and groundwater and devise appropriate techniques for reducing fluoride contamination and defluorination.

The one -dimensional mathematical model in Chapter 3 is based on the soil column experiment conducted in laboratory [4]. The experimental conditions considered medium to be isotropic and homogeneous with steady state. Also, initial and boundary conditions have been taken as per the soil column experiment [4]. The equations obtained have been solved using both analytical method and explicit finite difference scheme and it has been observed that analytical solutions offer a much better comparison as compared to numerical scheme.

As a result of the good comparison observed between experimental values and analytical results, the transport of fluoride ion in presence of different soil environment that is presence of different salts with hydroxyl ions has been studied in chapter 6 for steady as well as transient state and again a good comparison has been obtained between the experimental values and the values obtained through analytical solution of mathematical model.

The two-dimensional model has been presented in Chapter 4 as an extension of the one-dimensional mathematical model in order to assess and predict fluoride ion transport in longitudinal and transverse directions. The model is developed for isotropic, homogeneous and steady state conditions considering the flow velocity to be constant. The hypothetical study indicates that the effect of fluoride contamination is not uniform but decreases as we move away from origin along either longitudinal or transverse direction. In chapter 5 an attempt has been made to offer a new solution in the form of Laplace Adomian Decomposition method to understand the transport of a chemical ion in soil.

7.2 FUTURE SCOPE AND PROSPECTS OF THE WORK:

Mathematical models play important role in codifying the present knowledge and identifying the knowledge gaps, so as to help in assessment and prediction of contaminant transport. The proposed analytical solution presents an effective and useful model for further application to verify the newly developed numerical transport model for predicting the time-dependent transport of contaminants. The mathematical models, proposed in the study can be applied to field problems where the hydrological properties of the medium and prevailing boundary and initial conditions are the same as, or can be approximated by, the ones considered in this study.

However, the present model is not immune to amendment as the hydrological conditions considered for the medium and flow conditions are not ideal as in the study. The vadose zone is highly complex and is not a homogeneous and isotropic medium as considered in the study. The field situations are quite different from the laboratory conditions and therefore, the present model has its limitations in predicting confidently the presence of fluoride ion in a regional aquifer. Future works in developing a model for fluoride transport must include actual filed like situations. Also, the present mathematical model may be solved using different numerical schemes of finite difference and finite element or finite volume method and the results so obtained may be validated with the experimental or actual field like situations.

Plans for design and operation of the sitewide monitoring system of fluoride contamination and removal of fluoride can be supported by mathematical models that incorporate the uncertainties from alternative conceptual models. New results obtained by characterization of the vadose zone and monitoring can be used to test and improve the mathematical models.

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SUMMARY

The thesis is divided into seven chapters.

The first chapter gives an introduction about the soil characteristics, its composition, genesis. The solute transport processes for the transport of contaminants in soil and basic mathematical equations governing the transport of contaminant in soil with different possible solution techniques have been discussed. Thus, the need for a mathematical model, with an underlying physical concept, to assess its transport in soil and as a result in groundwater is necessitated.

The second chapter is about the review of literature undertaken for a comprehensive understanding of fluoride in soil. The different fluoride producing sources and factors affecting its availability in soil have been studied. The chapter also compiles the study of model for solute transport in rivers based on advection-dispersion equation for transport in the main channel with a sink term describing diffusive solute transfer to the hyporheic zone and the analytical solutions of one-dimensional solute transport problems with different initial and boundary conditions, in finite as well as semi-finite domain.

The third chapter entitled Mathematical Formulation and Solution for Fluoride Ion Transport in Soil studies the fluoride transport process modelled on the soil water column experiment conducted in the laboratory by Saxena and Rani. The soil column experiment is the study of leaching kinetics of F- by loading KF on undisturbed vertical soil column of the soil collected from Sambhar region of Rajasthan. In the soil column experiment soil columns were prepared surrounded by glass jacket of continuously flowing thermostat water. 60 g soil of pH 8.2 and of particle size (53>r) was gently packed at water filled porosity 0.315 cm^3/cm^3.

In each experiment, a fixed volume of aqueous salt solution (slug) with desired anion concentration (KF) was added at the top of the soil column and was allowed to get adsorbed uniformly in the column for 24 hrs, after which the column was continuously leached with de-ionized water or with other extractant as per requirement of the study [13]. The flow rate of extractant measured was constant (2+0.5 ml/10 min). Till the soluble anions were completely removed, leaching was carried out. After which, the column soil was transferred into the beaker in a known volume of extractant and his salt solution was stirred for 2 hrs. The ion concentration was further determined in the filtrate of the soil suspension to ensure the complete removal of soluble ions from the soil in the column. The total leachable concentration was taken equal to the total leachable concentration present initially during leaching (i.e. concentration t=0). The concentration of ions was determined in leachate collected periodically at an interval of 2 min, during each kinetic run.

While developing the mathematical model 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. Also, the application of fluoride as a contaminant is considered to be pulse type as per the laboratory experimental conditions. The contaminant is considered as degrading type with first order degradation.

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 is written as

$$\frac{\partial(\theta[F^-])}{\partial t} + \frac{\partial(\rho S)}{\partial t} = D\left\{\frac{\partial^2(\theta\,[F^-])}{\partial z^2}\right\} - q\frac{\partial[F^-]}{\partial z} - \theta k[F^-] \qquad (10)$$

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, $\rho =$ soil bulk density, $z =$ is vertical coordinate measured vertically downwards, $t =$ is time in sec.

The equation is solved analytically as well as numerically assuming pulse type boundary conditions with some initial concentration of fluoride already present in soil. The values of the parameters to be used are taken as used in soil column experiment. The analytical solution is obtained using the Laplace Transform technique. Because of the relatively small imposed mathematical boundary conditions, the analytical solution for a semi-infinite system should provide close approximations to analytical solutions that are applicable to physical well-defined system. The numerical solution of the one -dimensional advective–dispersive transport equation is obtained by employing an explicit finite-difference numerical technique by discretizing space and time, considering equilibrium sorption and first-order degradation for solute concentration in the solution phase. The results obtained both analytically and numerically for leachable fluoride remaining at time t in the soil column at different values of added fluoride are represented graphically. The pore volume and relative concentration profile for leached fluoride concentration are also represented graphically.

The study of graphs shows that analytical results are more comparable to experimental results as compared to the numerical results. The numerical simulation also exhibits a fair comparison of the experimental and simulated values. The one-dimensional model provides valuable insights into the processes that are involved in transport of fluoride in soil systems.

In realistic situations for example in an aquifer or field the transport of fluoride takes place in both vertically downward and horizontal direction. Therefore, in chapter 4, a two-dimensional model for fluoride transport in soil has been presented in which, the transverse component of velocity and dispersion coefficients are also considered along with the longitudinal components. The initial and pulse-type boundary conditions have been considered. The longitudinal and transverse seepage velocities have been taken to be constant. The properties of soil column experiment are extended to the two-dimensional model also and therefore in the model it is assumed that the soil medium to be homogeneous, isotropic saturated and of semi-infinite in horizontal plane. Since fluoride is reactive in nature and has the tendency to get adsorbed in the medium retardation factor and a first order decay term as a constant is also considered. Since, in the earlier chapter for one dimensional model, the analytical solution shows more comparison with observed experimental values, the solution for two-dimensional model is obtained analytically by employing Laplace Transform technique.

The concentration values of fluoride have been obtained from the analytical solution in the presence of initial fluoride concentration for a chosen set of numerical values of the different variables and represented graphically.

This study based on hypothetical numerical values of different parameters indicates that the effect of fluoride pollutant is not uniform but decreases as we move away from origin along either direction or horizontal plane. The proposed model and solution can be applied to field problems where the hydrological properties of the medium and prevailing boundary and initial conditions are the same as, or can be approximated by, the ones considered in this study.

The transport of fluoride, in presence of chemical moieties present in soil environment and groundwater, in porous media undergoes various chemical changes through advection, diffusion and dispersion. In addition, it involves other mechanisms like rate-limited sorption and desorption, biodegradation, and chemical reaction. In Chapter 5 a one-dimensional advection diffusion mathematical model to assess the transport of fluoride in presence of chemical moieties present in soil environment has been presented. The model is again based on the soil water column experiment for fluoride transport, wherein the soil column is loaded with Sodium Fluoride (NaF) and the presence of OH^- ions is varied by diluting the extractant with Sodium Hydroxide (NaOH), Potassium Hydroxide (KOH) and Ammonium Hydroxide (NH_4OH). In hydrolysis the chemical speciation of an organic contaminant gets changed. In this, as a result of the reaction of the fluoride salt with water, an exchange of some functional group from the salt with a hydroxyl (OH^-) group takes place. The extent of fluoride ion contamination attenuation by both bio degradation and hydrolysis depends on the chemical properties of the contaminant as well as the aqueous medium. The transformation processes in present case is shown to be following a first-order kinetic reaction. The experimental setup resembles the onsite conditions where presence of different salts in soil leads to change of pH of soil. The experimental conditions have been taken to be same as considered in chapter 3. 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.

However, in this chapter, the one-dimensional model is presented for vertical transient-state flow of water perpendicular to the soil layer and in order to compare the results with soil column experiment the steady state is considered as a special case. The transient flow of velocity has been considered exponential in one case and sinusoidal for another case. The solution of the model is obtained analytically and results obtained for leachable fluoride vs time have been plotted for steady state and transient state in presence of different hydroxides.

It has been observed that under transient flow conditions, for the exponential form of velocity, the leachable fluoride ion concentration decreases faster than in the sinusoidal form of velocity. The concentration levels for sinusoidal form of velocity are higher than that of exponential form of velocity.

From the results it is obtained that increased fluoride leaching takes place with increase in OH- concentrations as the radii of F^- and OH^- ions are comparable and an exchange of F^- and OH^- ions is inevitable. The cation attached to OH^- ion which affected F^- leaching significantly, the maximum being with Ammonium Hydroxide (NH_4OH) and minimum with Potassium Hydroxide (KOH). Ammonium NH_4^+ions which can carry at least 4 F^- ion through H-F bond [22] result in highest leaching as a result the leachable fluoride concentration is more in the order of KOH>NaOH>NH_4OH.

The analytical results obtained for steady state are in consonance with the experimental values and therefore offer good comparison. The model can be used to represent realistic conditions where field conditions are same as in the study.

Chapter 6 represents an attempt to model chemical ion transport through soil using Laplace Adomian Method. The effect of an external pressure / force in the form of gravitational force on flow through a porous medium has been studied by assuming the flow to be Newtonian. The chapter employs Laplace Adomian Decomposition Method to solve the equation for boundary layer flow of an incompressible fluid in the absence of pressure gradient. The rapidly converging analytical approximate solution of nonlinear ordinary or partial differential equation is given by decomposition method. The choice of operator determines the speed of convergence. The operator may be a highest-ordered differential operator or a combination of linear operators or a multidimensional operator. To handle the nonlinear terms, the method does not take the help of any simplification. The use of decomposition parameter is made only to group the terms. The study has been carried out for the flow in soil subject to external forces like gravity.

The extent of variation in the volumetric flow rate corresponding to different values of Reynolds number R_e= 1.0, 2.0, 3.0, 4.0 has been evaluated and graphically represented. The plots presented reveal that volumetric flow rate increases with a rise in the value of the Reynolds *Re*. The results show variation of the axial and transverse velocities in the channel flow of solute with change in Reynolds number R_e. The study is quite suitable for the application to the hydro-dynamical flow when it is subjected to the influence of an externally applied force. The solution to the nonlinear equations that govern the flow is obtained by using Adomian's decomposition method which is a powerful and efficient technique to get analytical approximate solution of nonlinear ordinary or partial differential equations and is rapidly convergent.

In chapter 7 future scope and prospects of the study have been discussed. The one-dimensional model presented in the study has offered good comparison with experimental results. However, the present model is not immune to amendment as the hydrological conditions considered for the medium and flow conditions are not ideal as considered in the study. The vadose zone is highly complex and is not a homogeneous and isotropic medium as considered in the study. The field situations are quite different from the laboratory conditions and therefore, the present model has its limitations in predicting confidently the presence of fluoride ion in a regional aquifer. Future works in developing a model for fluoride transport must include actual filed like situations. Also, the present mathematical model may be solved using different numerical schemes of finite difference and finite element or finite volume method and the results so obtained may be validated with the experimental or actual field like situations.

Plans for design and operation of the sitewide monitoring system of fluoride contamination and removal of fluoride can be supported by mathematical models that incorporate the uncertainties from alternative conceptual models. New results obtained by characterization of the vadose zone and monitoring can be used to test and improve the mathematical models.

Fluoride Ion Leaching Kinetics in Soil: A Mechanistic Model

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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

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

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	$1.48gm/cm^3$
θ	Water filled porosity θ	$0.315cm^3/cm^3$
k	First order degradation constant	$0.00414/sec$
V	Pore water velocity	$0.75cm/sec$

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.

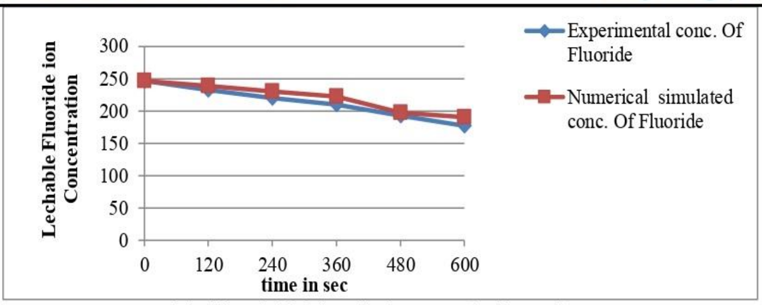

Fig.1 Leachable Fluoride ion concentration vs time

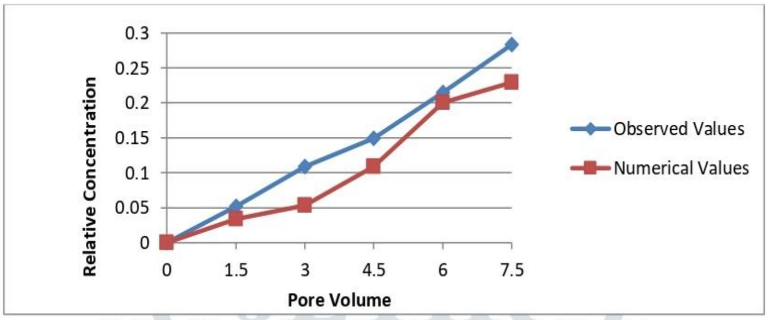

Fig.2 Pore Volume vs Relative Concentration of Leached Fluoride ion

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.

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Laplace Adomian Decomposition Method to study Chemical ion transport through soil

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Abstract

The paper deals with a theoretical study of chemical ion transport in soil under a uniform external force in the transverse direction, where the soil is taken as porous medium. The problem is formulated in terms of boundary value problem that consists of a set of partial differential equations, which is subsequently converted to a system of ordinary differential equations by applying similarity transformation along with boundary layer approximation. The equations hence obtained are solved by utilizing Laplace Adomian Decomposition Method (LADM). The merit of this method lies in the fact that much of simplifying assumptions need not be made to solve the non-linear problem. The decomposition parameter is used only for grouping the terms; therefore, the nonlinearities is handled easily in the operator equation and accurate approximate solution are obtained for the said physical problem. The computational outcomes are introduced graphically. By utilizing parametric variety, it has been demonstrated that the intensity of the external pressure extensively influences the flow behavior.

Keywords: Porous medium; Adomian's decomposition method; Laplace transformation, Reynolds number

MSC 2010 No.: 35A25, 35Q40

1. Introduction

Most of the phenomena occurring in nature are non-linear. In the biological world, non-linearity is a common problem. Modelling different problems of soil science, for example, fluid flow in soil involves nonlinear partial differential equations. Khuri (2001) proposed a numerical Laplace decomposition algorithm to solve a class of nonlinear differential equations. Yusufoglu (2006) applied this method for the solution of Duffing equation. Nasser and Elgazery (2008) used this method to solve Falkner-Skan equation. The numerical system essentially outlines how the Laplace Transform might be utilized to solve the nonlinear differential equations by utilizing the decomposition technique.

For solving a certain class of problems, it is found that application of a combination of Laplace transform method and Adomian decomposition method namely Laplace Adomian decomposition method (LADM) is very useful. Some further discussion on this method has been made by Babolian et al. (2004) and Biazar et al. (2004). The method was used by Wazwaz (2010) in handling Volterra integro-differential equations and by Dogan (2012) for solving a system of ordinary differential equations. Jafari and Jassim (2015) discussed numerical solutions of telegraph and Laplace equations on cantor sets using local fractional Laplace decomposition method. Pirzada and Vakaskar (2015) discussed solution of fuzzy heat equations using Adomian Decomposition method.

In the present paper, the effect of an external pressure / force on flow through a porous medium has been analysed by assuming the flow to be Newtonian as studied by Raptis and Perdikis (1983) and Sacheti (1983). The analysis is carried out by employing Laplace Adomian Decomposition Method as discussed by Adomian (1986) and Adomian and Cherruault (1993), Adomian and Cherruault (1995) and some important predictions can be made on the basis of the present study. The advantage of decomposition method is to give analytical approximate solution of nonlinear ordinary or partial differential equation which is rapidly convergent as shown by Adomian and Cherruault (1993), Adomian and Cherruault (1995). The speed of convergence depends upon the choice of operator which may be a highest-ordered differential operator or a combination of linear operators or a multidimensional operator. This method does not take the help of any simplification for handling the nonlinear terms. Since the decomposition parameter is used only for grouping the terms, therefore, the non-linearities can be handled easily in the operator equation and accurate approximate solution may be obtained for any physical problem. The study has been carried out for the flow in soil subject to external forces like gravity.

2. Mathematical Modeling of the Problem

Nomenclature: (x, y) : Cartesian coordinates of a point, (u, v): Velocity components along x- and y- directions, U_0 : Characteristic velocity, F_0 : Applied external force, k : Permeability of porous matrix, h : Half-width of channel, η : Non-dimensional distance, μ: Coefficient of viscosity, v : Kinematic viscosity of solute, ρ : Density of solute, R_e : Reynolds number.

A transport system mainly consists of three-dimensional (3D) vessels. However, in some cases, such as in micro-vessels of soil it is approximately 2D and it can be considered as channel flow. A physical sketch of the geometry is shown in Figure 1. The x-axis is taken along the centre line of the channel, parallel to the channel surface and y-axis in the transverse direction. The flow is taken to be symmetric about x-axis as studied by Sharma (2016).

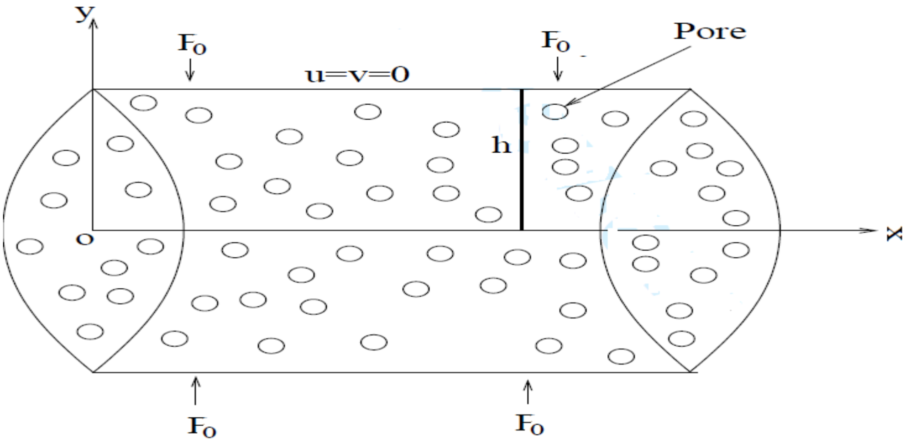

Figure 1: Physical Sketch of the Problem

However, the solutions of multidimensional transient flow of any solute can be obtained by numerical modeling, their applications are limited in the field. From a hydrological perspective, Pirzada and Vakaskar (2015) discussed that solute movement in soil and its spatial distribution can largely be controlled by the water fluxes of the groundwater. For an improved understanding of the magnitude of these fluxes, accurate estimates of the temporal and spatial water uptake patterns are needed.

Let u and v be the velocity components along x- axis and y-axis respectively and F_0 be the applied external pressure. In the absence of pressure gradient, the equation for boundary layer
flow of an incompressible fluid is

$$u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}=\upsilon\frac{\partial^2 u}{\partial y^2}-\frac{\upsilon}{k}u-\frac{F_0^2 u}{\rho}, \qquad (11)$$

and the continuity equation is

$$\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}=0, \qquad (12)$$

where ρ the density of solute, υ is the kinetic coefficient of viscosity and k denotes the permeability of the porous medium. Assuming that the flow is symmetric about the central line $y=0$ of the channel, we focus our attention to the flow in the region $0 \le y \le h$ only. Then the boundary conditions to be taken care of are as follows:

$$u=v=0 \quad at \;\; y=h, \qquad (13)$$

and

$$\frac{\partial u}{\partial y}=0, v=0 \quad at \;\; y=0. \qquad (14)$$

We now introduce the non-dimensional quantities defined by

$$\zeta=\frac{x}{h}\;, \qquad \eta=\frac{y}{h}\;, \qquad u=\frac{U_0}{h}f'(\eta), \qquad v=-U_0\,f(\eta), \qquad (15)$$

where U_0 is the characteristic velocity.

It may be noted that the continuity equation (2) is automatically satisfied.
In terms of the non-dimensional variables, Equation (1) reads

$$f'''+R_e(ff''-f'^2)-f'H=0. \qquad (16)$$

Where R_e and K are the Reynolds number and porosity permeability parameter respectively, defined by

$$R_e=\frac{U_0 h}{\nu}, K=\frac{k}{h^2}\;, H=\left[F_0^2+\frac{1}{K}\right]. \qquad (17)$$

With the use of transformation (5), the boundary conditions (3) and (4) become

$$f'=f=0 \quad at \;\; \eta=1, \qquad (18)$$

and

$$f=f''=0 \quad at \;\; \eta=0. \qquad (19)$$

The equation (6) reduces to

$$f'''-f'H=0,$$

when Reynolds number R_e is zero and have solution of the form

$$f=C_1+C_2e^{a\eta}+C_3e^{-a\eta},$$

where $a=\sqrt{H}.$

At $\eta = 0, f = 0, f'' = 0$, gives $C_1 + C_2 + C_3 = 0$ and $a^2C_2 + a^2C_3 = 0$.

implying

$$f = 2C_2 sinha\eta,$$

and

$$f' = 2aC_2 cosha\eta.$$

If $\eta = 0$ and $f'(0) = b$

$$f = \frac{b}{a} sinha\eta. \tag{20}$$

3. Analysis of the Model

In this section, in order to analyse the model, we first solve equation (6) subjected to the boundary conditions (8) and (9). For this purpose, we use the Laplace Adomian Decomposition Method (LADM) as shown by Turkyilmazoglu (2015) and Turkyilmazoglu (2017). In the first step, we consider the Laplace transformation of equation (6), whereby we get

$$L[f'''] + R_e L[ff'' - f'^2] + HL[f'] = 0, \tag{21}$$

Here and in the sequel, L[F] stands for the Laplace transform of the function F.

Using the property of the Laplace transform, we have

$$s^3L[f] - s^2f(0) - sf'(0) + R_e L[ff' - f'^2] - H[sL[f] - f(0)] = 0 \tag{22}$$

Using the boundary condition (9), from equation (12) we obtain

$$s(s^2 - H)L[f] = -R_e L[ff'' - f'^2] + sf'(0), \tag{23}$$

Writing $f'(0) = b$ (where b is a constant), equation (13) assumes the form

$$L[f] = \frac{b}{s^2 - H} - \frac{R_e}{s(s^2 - H)} L[ff'' - f'^2]. \tag{24}$$

Following Adomian Decomposition Method, we assume the solution for f in the form of an infinite series:

$$f = \sum_{n=0}^{\infty} f_n, \tag{25}$$

To write it in the form

$$\phi(\eta) = ff'' - f'^2 \ ; \ \phi(\eta) = \sum_{n=0}^{\infty} A_n, \tag{26}$$

where $A_n = A_n(f_0, f_{1,\ldots\ldots,} f_n)$, are the so-called Adomian polynomials [Adomian (1986)] . To find A_n, we introduce a scalar λ such that

$$f(\lambda) = \sum_{n=0}^{\infty} \lambda^n f_n, \tag{27}$$

The parameter λ ,used in (17) is not a perturbation parameter; it is used only for grouping the terms of different orders. Thus, the parameterized form of (16) is given by

$$\phi(\lambda) = \sum_{n=0}^{\infty} \lambda^n \left(\sum_{i=0}^{\infty} f_i f''_{n-i} - \sum_{i=0}^{\infty} f'_i f'_{n-i} \right). \tag{28}$$

From the definition of Adomian polynomials, it follows that

$$A_n = \frac{1}{n!} \frac{d^n}{d\lambda^n} (\phi(\lambda))_{\lambda=0}. \tag{29}$$

Now substituting (18) into (19), we get

$$\begin{gathered} A_0 = f'_0 f_0 - f'^2_0, \\ A_1 = f_0 f''_1 + f_1 f''_0 - 2 f'_0 f'_1, \\ A_2 = f''_0 f_2 + f''_1 f_1 + 2 f'_0 f''_2 - f'^2_1, \\ A_3 = f''_0 f_3 + f''_1 f_2 + f''_2 f_1 - f'_3 f_0 - 2 f'_0 f'_3 - 2 f'_1 f'_2 \, , \end{gathered} \tag{20}$$

and so on. Substitution of equations (15) and (16) into the equation (14), further yields

$$L\left[\sum_{n=0}^{\infty} f_n \right] = \frac{b}{s^2 - H} - \frac{R_e}{s(s^2 - H)} L\left[\sum_{n=0}^{\infty} A_n \right]. \tag{21}$$

Matching both sides of equation (21) yields the iterative algorithm:

$$L[f_0] = \frac{b}{s^2 - H}, \tag{22}$$

$$L[f_1] = -\frac{R_e}{s(s^2 - H)} L[A_0], \tag{23}$$

$$L[f_2] = \frac{R_e}{s(s^2 - H)} L[A_1], \tag{24}$$

$$L[f_3] = \frac{R_e}{s(s^2-H)} L[A_2], \tag{25}$$

and so on. Now considering the inverse Laplace transform of equation (22) the following value of f_0 is obtained for $a = \sqrt{H}$:

$$f_0 = \frac{b}{a} \sinh(a\eta) \, . \tag{26}$$

The first Adomian polynomial A_0 calculated from eqns. (20) and (26) is found in the form

$$A_0 = -b^2. \tag{27}$$

Since $L[A_0] = [-b^2] = -\frac{b^2}{s}$; by applying Laplace inversion, we obtain

$$f_1 = \frac{b^2 R_e}{a^2}\left(\frac{1}{a}\sinh(a\eta) - \eta\right). \tag{28}$$

Proceeding in a similar manner, using (20) and (28), we calculate the second Adomian polynomial A_1 given by

$$A_1 = -\frac{2b^2 R_e}{a^2} - \frac{b^3 R_e}{a}\eta\sinh(a\eta) + \frac{2b^3 R_e}{a^2}\cosh(a\eta). \tag{29}$$

Next, we find the Laplace transformation of A_1 given by (29), substitute it in (24) and then consider Laplace inversion. Thus, we have found the expression of f_2 given below.

$$\begin{aligned} f_2 = \frac{2b^3 R_e}{a^2}\Bigg[\frac{1}{a^2}\Bigg(&\frac{1}{a}\sinh(a\eta) - \eta - \frac{1}{2a^2}(\eta\cosh(a\eta) - \frac{\sinh(a\eta)}{a} \\ &+ \frac{1}{8}(\eta^2\sinh(a\eta) - \frac{3}{a}(\eta\cosh(a\eta) - \frac{\sinh(a\eta)}{\eta})\Bigg)\Bigg], \end{aligned} \tag{30}$$

If we consider three-term approximation of the solution

$$f = f_0 - f_1 - f_2, \tag{31}$$

By taking $\lambda = 1$; the calculated expression for f reads

$$\begin{aligned} f(\eta) = \frac{b}{a}\sinh(a\eta) &+ \frac{b^2 R_e}{a^2}\left(\frac{\sinh(a\eta)}{a} - \eta\right) \\ &+ \frac{2b^3 R_e^2}{a^2}\Bigg(\frac{1}{a^2}\left(\frac{3}{2a}\sinh(a\eta) - \eta - \frac{1}{2}\cosh(a\eta)\right) \\ &+ \frac{1}{8}\left(\eta^2\sinh(a\eta) - \frac{3}{a}(\eta\cosh(a\eta) - \frac{\sinh(a\eta)}{a})\right)\Bigg). \end{aligned} \tag{32}$$

The results coincide with equation (10) when Reynolds number is zero.

The first derivative of $f(\eta)$ is given by

$$\begin{aligned} f'(\eta) = bcosh(a\eta) &+ \frac{b^2 R_e}{a^2}(\cosh(a\eta) - 1) \\ &+ \frac{2b^2 R_e^2}{a^2}\Bigg(\left(\frac{3}{a}\eta\cosh(a\eta) - \frac{\sinh(a\eta)}{a} - 1\right) \\ &+ \frac{a^2}{8}(\eta^2\,\mathrm{acosh}(a\eta) - \eta\sinh(a\eta)\Bigg). \end{aligned} \tag{33}$$

Now using the boundary condition $f_1'(1) = 0$, we can obtain the expression for b in the form

$$b = \frac{-(cosha - 1) + \sqrt{4sinh^4 a + a\left(2 + \frac{a}{2}\right) + sinha + (a^3 - 8)cosh2a - 12c}}{4\frac{R_e}{a^2}\left(\frac{3}{2}cosa - \frac{a}{2}sina - 1 + \frac{a^3}{8}cosa - \frac{a^2}{8}sina\right)} \tag{34}$$

The volumetric flow rate is then given by

$$V_m = 2\int_0^1 f'(\eta)d\eta\,, \tag{35}$$

$$= 2\left[\frac{bsinha}{a} + \frac{b^2}{a^2}R_e\left(\frac{sinha}{a} - 1\right) + \frac{b^3R_e}{a^4}\left(\frac{3sinha}{a} - cosha - \frac{3}{2}\right) + \frac{a^2}{2}\left(\left(1 + \frac{3}{a^2}\right)sinha - \frac{3}{a}cosha\right)\right]. \tag{36}$$

$f''(1)$ can be obtained by differentiating equation (33) and then considering $\eta = 1$

4. Results and Discussion

We now present here the important results from our work in terms of pertinent dimensionless parameters. However, for practical considerations, we also mention some typical values of the corresponding dimensional parameters, as appropriate to the results subsequently obtained.

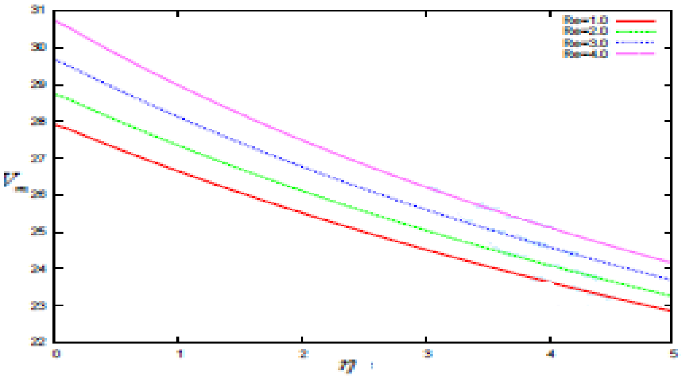

Figure. 2: Distribution of $V_m$with η different values of Reynolds numberR_e

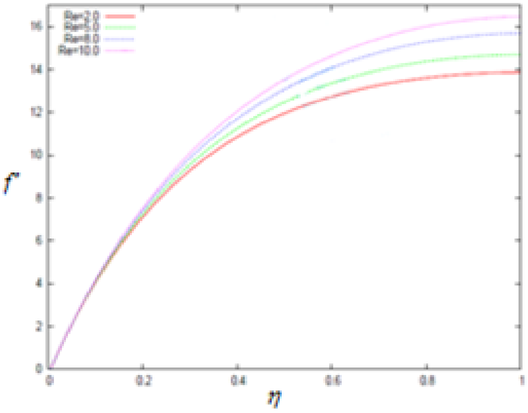

Figure 3: Distribution of f' with η for different values of Reynolds number R_e

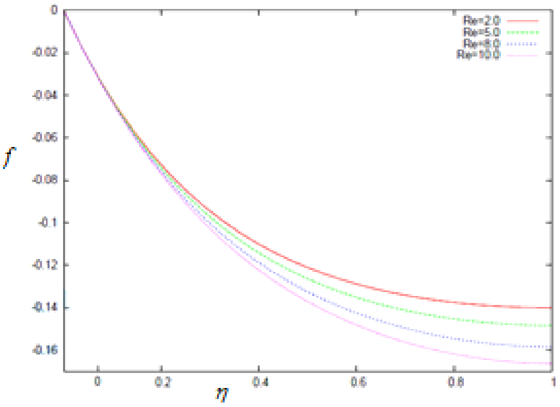

Figure 4: Distribution of f with η for different values of Reynolds number R_e

In finding the estimates, we have taken density, ρ = 1440$kg.m^{-3}$, viscosity of the solute μ = $10^{-3}kg.m^{-1}s^{-1}$. Figure 2 illustrates the extent of variation in the volumetric flow rate corresponding to different values of Reynolds number R_e= 1.0, 2.0, 3.0, 4.0. The plots presented in this figure reveal that volumetric flow rate increases with a rise in the value of the Reynolds *Re*. The variation of f' and f with η are shown in Figure 3 and Figure 4 respectively.

5. Concluding Remarks

The numerical results estimated are presented graphically in Figures 2-4. These figures illustrate the variation of the axial and transverse velocities in the channel flow of solute with change in Reynolds number R_e.

The present study deals with a theoretical investigation of solute flow through a porous soil under the action of an external force. The study is quite suitable for the application to the hydro-dynamical flow when it is subjected to the influence of an externally applied force. The solution to the nonlinear equations that govern the flow is obtained by using Adomain's decomposition method which is a powerful and efficient technique to get analytical approximate solution of nonlinear ordinary or partial differential equations and is rapidly convergent as studied by Adomian and Cherruault (1993) and Cherruault et al (1995).

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