Chapter 1

Introduction

1.1 Porous Media

A porous medium is a domain which contains a solid matrix with an interconnected or disconnected voids. These voids may be distributed within a regular or random pattern. Here solid materials include this synthetic polymers, organic materials like the kidney and lung tissue matrices and the void space is occupied with fluid phases, such as liquid or gas. There are different forms of porous medium, for example fissured rock, sand, cemented sandstone, etc, are naturally porous medium, where as organic porous medium include things like lungs, kidneys, bones etc and manufactured porous medium include things like foam rubber, paper, bread and ceramics etc. Pigments, ceramics, membranes, catalysts, electrodes etc are very useful medium which is used in a numerous industrial and engineering fields like diper and paper industries, hydrogeology, petroleum reservoir engineering and biomedical engineering. Although the porous medium can have many different geometrical characteristics, we only take into account two in order to examine flow through them mathematically:

(1) porosity

(2) permeability.

1.1.1 Porosity

The percentage of the total volume of a porous media which is made up of void volume is known as the porosity of the medium, i.e.

$$Porosity = \frac{Total\ void\ volume}{Total\ volume\ occupied\ by\ solid\ matrix}$$

The definition of porosity is predicted on the idea that all of the void space is interconnected where as effective porosity is the fraction of a connected void to total volume. Porosity in natural media is limited to 0.6.

1.1.2 Permeability

The term "permeability" refers to the characteristic of porous media that indicates how easily a fluid may be forced to pass through it by applying a pressure gradient. When a porous media is made up of solid spheres with a diameter of d, its permeability K is determined by $K = d^2e^2/180(1-\epsilon)^2$, where e represents the porosity of the porous medium and ϵ denotes the constant [2]. When permeability varies with location then the medium is said to be heterogeneous and if permeability varies with flow direction, the medium is considered as anisotropic.

1.2 Background of Porous Media

From 18th to 19th centuries, the geometry of porous bodies, fundamental principles of mechanics and volume fraction concept are some essential parts of porous media theory. In 1762, Leonhard Euler made a remark on porous bodies in his published work "Anleitung zur Naturlehre". After that an important contribution

to the porous media theory was made by Reinhard Woltman (1754-1837). He presented some useful idea on soil mechanics, porous media and the concept of volume friction, etc. The trasient process of heat conduction described by a partial differential equation, was first formulated by Jean Baptiste Joseph Fourier (1768-1830) and he opened up new areas of investigation in mathematical physics with his 1807 masterpiece, Theorie de la Propagation de la Chaleur dansles Solides. It would be another accessible to the general scientific commumity through publication of his classic monograph, Theorie Analytique de la Chalur (Analytic Theory of Heat [Fourier, 1822]) [3]. In 1848, Delesse [4], presented that the surface friction is equal to volume friction of a saturated porous body under certain conditions. In 1855, Fick [5], presented the theory of mixture for a diffusion problem. In 1871, Stefan [6] discussed the theory of mixture for two gases. In 1856, Darcy [7], demonstrated a result related to the loss of pressure and total volume of running water through the porous media (saturated sand). In the 19th to 20th centuries, many researchers contributed in the development of porous media theory, some of them are Jaumann [8], Fillunger [9], Heinrich [10], Biot [11], Boer and Ehlers [12], Kelly [13], Adkins [14] , Bowen [15], etc. In 1980, Bowen [16] discussed a model for incompressible and compressible porous media, which was based on the theory of mixture. In 1989, Ehlers [17] proposed a new concept related to the component of porous media to overcome the confusion related to the grading of material. In recent times, there are many fields in which the theory of porous media arises, for example, stability analysis of partially and fully saturated soils, construct of dams, electronics cooling, tissue engineering, nuclear waste repository, etc.

1.3 Diffusion

The term "diffusion" originates from the Latin language and its meaning is "to spread out". The process of moving atoms or molecules from one system to another via random molecular motions is known as diffusion. This process results in a uniform dispersion of matter or material atoms and is not caused by any forceful activity. The mechanisms of diffusion occur in gases and liquids through Brownian motion and in solids through interstitial diffusion or vacancy. Concentration gradient is the root cause or driving force of this diffusion phenomenon. The mass transfer process is connected to the diffusion phenomenon, and mass transfer occurs when a mixture of substances moves through a medium from one point to another. Mass transfer causes the diffusion or convection process to occur. Therefore, mass transfer in a fluid or stationary solid under a concentration gradient is considered the diffusion process. For the normal diffusion process, the governing equation has the following form:

$$\frac{\partial u}{\partial t} = D\Delta u, \tag{1.1}$$

where u is the concentration of the solute, D is the diffusion coefficient of the dependent variable, t is the time and Δ is the Laplace operator.

In a normal diffusion, a particle moves randomly, and has a mean square displacement (MSD) proportional to time (MSD $\propto$ time), as demonstrated by Einstein's theory of Brownian motion. From the literature, it is observed that the normal diffusion process is not able to describe some complex diffusion procedures, for example, diffusion in heterogeneous medium (porous media). To describe anomalous diffusion processes, diffusion equations with fractional derivatives play an important role. As

fractional calculus research advances [18], [19], [20], it is observed that the anomalous diffusion is described by a power law in which MSD for the anomalous diffusion is proportional to t^w (a non-linear relationship between the MSD and time), where w is either greater or smaller than one. If w is less than 1, the particles undergo a sub-diffusion process. This can happen due to crowding or walls. Example of sub-diffusion process can be seen in protein diffusion within cells, or diffusion through porous media. If $1 < w < 2$ then the particles undergo a super diffusion process. Super-diffusion processes occurs due to the active cellular transport processes or due to jumps with a heavy-tail distribution.

1.3.1 Application of Diffusion Equations

The application of diffusion process can be seen in many areas of science, medical and engineering as described below:

Medical Sciences

The diffusion equation, essential for describing the spread of particles and substances, finds numerous applications in medical sciences [21], [22], [23]. Its role is critical in understanding and optimizing various physiological and pathological processes:

- **Drug Delivery Systems:** The diffusion equation models the release and distribution of drugs within the body [24]. This is particularly important for controlled-release formulations, ensuring that therapeutic agents reach targeted tissues at desired rates and concentrations.

- **Tissue Engineering:** In the development of artificial tissues and organs, the diffusion equation models nutrient and oxygen transport within scaffolds [25].

This ensures that cells receive adequate sustenance for growth and function, which is crucial for the viability of engineered tissues. Cancer Research: The equation is used to study the diffusion of therapeutic agents within tumors. Researchers can optimize treatment strategies to enhance drug efficacy and reduce side effects by understanding how drugs penetrate and spread in cancerous tissues.

- **Neuroscience:** The diffusion equation is used to study the spread of neurotransmitters and other molecules in the brain [26]. This helps in understanding neural signaling pathways and developing treatments for neurological disorders.

- **Biomedical Engineering:** In the design of medical devices and implants, the diffusion equation models the release of therapeutic agents from coatings and the transport of substances through biomaterials. [27] This ensures the effective and safe performance of medical devices. Through these applications, the diffusion equation provides critical insights into the transport phenomena underlying numerous physiological processes and medical treatments, contributing to advancements in medical science and healthcare.

Economics

In economics, diffusion equations are used to model the spread and adoption of new technologies, innovations, and information across markets and populations [28], [29]. These models help economists to understand how new products or technologies penetrate markets, predicting adoption rates and market saturation. They are crucial in studying the diffusion of innovations, where the equation helps to forecast the adoption curve based on factors such as social influence, market conditions, and consumer behavior.

Environmental Sciences

In environmental sciences, diffusion equations are essential for modeling the transport and dispersion of pollutants in air, water, and soil [30], [31]. They are used to predict how contaminants spread from sources such as industrial discharges, agricultural activities, and urban runoff, helping to assess environmental impacts and risks. In air quality studies, diffusion equations model the dispersion of pollutants and greenhouse gases, aiding in the development of strategies to control air pollution and mitigate climate change. In water bodies, these equations help understand the diffusion of nutrients, chemicals, and microorganisms, informing the management of aquatic ecosystems and the prevention of eutrophication. Soil contamination studies use diffusion equations to predict the movement of hazardous substances through the soil, guiding remediation efforts and land use planning. Overall, by providing insights into the behavior of pollutants in various environmental media, diffusion equations support the development of effective environmental protection and management strategies.

Geological Sciences

In geological science, diffusion equations are fundamental for modeling the transport of heat, solutes, and gases through the Earth's crust and subsurface environments [32], [33]. They are crucial in understanding geothermal gradients, aiding in the exploration of geothermal energy by predicting how heat diffuses through rock formations. These equations also help in analyzing the migration of contaminants in groundwater, providing insights for environmental protection and remediation efforts. Additionally, diffusion equations are used to study the diagenesis of sedimentary rocks, where the movement of chemical species affects mineral transformations over geological timescales. By modeling these processes, diffusion equations enable

geologists to better predict and manage natural resources, assess environmental impacts, and understand the Earth's thermal and chemical evolution.

Groundwater Hydrology

In groundwater hydrology, diffusion equations are crucial for modeling the movement and dispersion of contaminants and solutes in aquifers. They help in predicting how pollutants spread through groundwater systems, which is essential for assessing the impact of spills, agricultural runoff, and industrial discharges on water quality. These equations also aid in designing and optimizing remediation strategies for contaminated groundwater by simulating the effectiveness of various cleanup methods. Additionally, diffusion equations are used to study the transport of nutrients and other dissolved substances, contributing to the management and protection of water resources. Hydrologists can better predict and manage groundwater flow and quality by understanding the dynamics of solute transport through porous media, ensuring safe and sustainable water supplies.

Groundwater is one of the most important sources for living on earth, and also the basic needs for industries and agriculture. Now a days, increasing pollution is becoming a serious issue for human and nature. Groundwater contamination is dangerous not only for healthy environment but also damage long term exposure. Pollution in groundwater [34], [35], [36], [37], [38] can occur due to the leakage in sewers, over fertilizing in agriculture, leakage through septic tank waste, etc. Many countries have been taken different action to remediate the groundwater but it is more difficult and expensive. The transport of pollution in the groundwater is explained for different mechanisms, like diffusion, precipitation, percolation, absorption, decay, etc. The subsurface movement of contaminants is highly complex and difficult

to anticipate. For each type of contamination, the reaction with geological materials takes a distinct form. The two primary feature via which dissolved solutes are transported are diffusion and advection. Advection and diffusion are both transport mechanisms, but they differ in how they move substances. In advection, a substance is transported by the bulk motion of a fluid, such as water or air and in diffusion, a substance moves without the bulk motion of a fluid. Diffusion is a time-dependent process that occurs due to the random motion of individual particles. Another important feature of a pollutant for groundwater contamination is its solubility. By using both advection and dispersion, groundwater moves from regions with higher hydraulic head to areas with lower hydraulic head, carrying dissolved solutes. The bulk transport of solutes carried by groundwater in motion is referred to as advection. The term "diffusion/dispersion" describes how the pollutant plume moves from locations of high concentration to areas of lower concentration. Diffusion and dispersion are both processes that involve spreading something out. Diffusion is caused by random molecular motions, such as Brownian motion. It's a microscopic phenomenon and Dispersion can be caused by non-ideal flow patterns and is a macroscopic phenomenon. The pollutants travel in both longitudinal and horizontal directions and move vertically downward to the bottom of the groundwater, and disperse according to the solute concentration's coefficient. The mathematical model governing the process transportation of solute in groundwater is explained by reaction-advection-diffusion equation.

1.3.2 Reaction-advection diffusion equation

The mathematical modeling of the transportation of solute in groundwater has plenty of scope for research. Many research studies have applied many methods

to analyze the problem of groundwater contamination. Predicting the solute concentration in lakes, streams, aquifers, and rivers can also be done with the help of solute transport modeling. Scientists and engineers have provided a plethora of mathematical models for solute transport in groundwater [39], [40], [41], [42]. Groundwater modeling has been the primary tool for researchers and hydrologists, and it is useful to analyze resource potential and forecast future environmental effects under various scenarios. These studies have advanced our understanding of solute transport patterns in porous media, and raised some problems about pollution of the subsurface environment. Partial differential equations (PDEs) play an important role to represent a wide range of natural systems, including the thermal pollution of river systems, smoke and dust-induced air pollution, and groundwater pollution.

The equations describing flows in porous media are nonlinear, the diffusion and advection are the main factors. The advection-diffusion equation (ADE) describes solute transport when advection and diffusion act together. The reaction-advection-diffusion equation (RADE) is a different variant of the chemical equation that occurs with a reaction term if the chemical being carried through medium is reactive. Numerous fields, including biology, mechanical engineering, environmental engineering, petroleum engineering, chemical engineering, heat transport, and soil sciences, have extensively involved RADEs. The general solute transport model of reaction-advection-diffusion equation given by [43], [44], [45]

$$\frac{\partial u}{\partial t} = \bigtriangledown.(D \bigtriangledown u) - V \bigtriangledown u + \kappa f(u) \tag{1.2}$$

where V is the velocity vector. κ is real coefficient and $f(u)$ is reaction term.

The solute concentration profiles showed skewness, abrupt leading edges, and quicker

than Fickian growth rates for the solute transport in extremely heterogeneous mediums. Conventional solute/mass transfer models are unable to predict these consequences. In highly heterogeneous media, the anomalous nature of solute transport can be simulated using fractional differential equations. The complex heterogeneous structure of the rock matrix, which can be assumed as a fractal, and the intricate processes of solute absorption on the solid matrix are primarily responsible for the anomalous nature of diffusion. Fomin demonstrated mathematically that diffusion on fractals should be represented by a fractional differential equation, the order of which is dependent on the dimension of the fractal medium. Several writers demonstrated that the CTRW converges to fractional-order differential equations in the asymptotic case (long times and/or distances). Fractional differential equations have been effectively used to describe anomalous diffusion events in a variety of fields. These equations can be considered as the long-time and long-space limit of CTRW. From the literature survey, it is can be seen that reaction-advection-diffusion equation with time-space fractional derivative are a useful tool for modeling the non-Fickian anomalous mass/solute transport processes through the heterogeneous porous medium.

1.4 Fractional Calculus

Research on differential calculus and its applications is highly significant and well-established. Additionally, we know the concept of the n^{th} order derivative, which denotes that, for a given positive integer n, the differential operator must apply on the differentiable function n times in succession. Fractional calculus became known when G. de L'Hospital and G. W. Leibniz considered the idea that n might not be an integer in 1965. Following that day, a large number of academics investigated

this matter and made contributions to the field of fractional calculus. Some of them are L. Euler, Laplace, Lagrange, S. F. Lacroix, J. Fourier, N.H. Abel, J. Liouville, etc. In addition, B. Riemann, H. Weyl, G. Leibniz, A. K. Grunwald, and A.V. Letnikov have all contributed to fractional calculus. From the 18^{th} to 19^{th} century, the literature of arbitrary order derivative is missing from the field of mathematics. In this period, the derivative of an arbitrary order was only mentioned by L. Euler and J. Fourier but they did not use in their further work. In the 19^{th} century, S. F. Lacroix used the Gamma function to determine the derivative of an arbitrary order of a function x^m. The result is stated as

$$D_x^{\alpha} x^m = \frac{\Gamma(m)}{\Gamma(m-\alpha)} x^{m-\alpha}. \tag{1.3}$$

In a published work in 1823, Ross provided an evolution of the fractional derivative in fractional calculus. This book also involves the solution of a Tautochrone problem using the fractional derivative by N. H. Able. In 1832, J. Liouville provided a logical formulation for the derivative of fractional order for any arbitrary function by expanding it into an exponential series. After that, there were numerous disagreements on the meaning of fractional order derivatives between 1835 and 1850. However, a distinct definition of the fractional order derivative involving the definite integral was provided by G. F. Bernhard Riemann in 1853. Using Cauchy's integral formula, Sonin [46] defined the differentiation of arbitrary order. Laurent [47] produced the Riemann-Liouville fractional order derivative later in 1884. M. Caputo made the most substantial addition to fractional calculus in 1967. His work addressed a critical flaw in Riemann-Liouville's definition of the fractional derivative. As time passed, many scholars expressed their interest in fractional calculus, and numerous authors presented different books. Some of those are Nishimoto [48], Miller and Ross [49], Kiryakova [50], Rubin [51], Podlubny [52], Hilfer [53], Kilbas

et al. [54], etc. The next sub-section include the definition of the Fractal Integral, Riemann-Liouville derivative and Caputo derivative and it's properties used in this thesis [55].

1.4.1 The Fractal Integral

Definition 1.1. According to the Riemann-Liouville approach to fractional calculus the notion of fractional integral of order α ($\alpha > 0$) is a natural consequence of the well known formula (usually attributed to Cauchy), that reduces the calculation of the n-fold primitive of the function $\gamma(x)$ to a single integral of convolution type. In our notation the Cauchy formula reads

$$J^n\gamma(x) = \gamma_n(x) = \frac{1}{(n-1)!}\int_0^t (t-\tau)^{n-1}\gamma(\tau)d\tau, t > 0, n \in N,$$

where N is the set of positive integers. From this definition, we note that $\gamma_n(x)$vanishes at $t = 0$ with its derivatives of order 1,2,...,$n-1$.

1.4.2 Riemann-Liouville derivative of Fractional Order

Definition 1.2. The Riemann-Liouville derivative of arbitrary order $\alpha \geq 0$ of the function $\gamma(x)$ is defined as

$${}_aD_t^\alpha\gamma(x) = \begin{cases} \frac{1}{\Gamma(k-\alpha)}\frac{d^k}{dt^k}\int_c^t (t-y)^{k-\alpha-1}\gamma(y)dy, & \alpha > 0, \\ \gamma(x), & \alpha = 0, \end{cases}$$

where $t > a$, t, a, $\alpha \in R$, $k-1 \leq \alpha < k$.

1.4.3 Caputo Derivative of Fractional Order

Definition 1.3. Let us consider, γ:$\mathbf{R} \to \mathbf{R}$, x $\to \gamma(x)$, then the Caputo fractional derivative of order α is defined as

$$ {}_0^C D_x^\alpha \gamma(x) = \begin{cases} \frac{1}{\Gamma(m-\alpha)} \int_0^x (x-y)^{m-\alpha-1} \gamma^{(m)}(y) dy, & m-1 < \alpha < m, \\ \gamma^{(m)}(x), & \alpha = m, \end{cases} $$

where $m \in N$ and N is the set of natural number.

Property 1. Let $\gamma(x) = C$, where C is a constant, then

$$ {}_0^C D_x^\alpha \gamma(x) = 0. \tag{1.4} $$

Property 2. Let $\gamma(x) = Cx^n$, where $n \geqslant 1$ and C is a positive real constant then

$$ {}_0^C D_x^\alpha \gamma(x) = C \frac{\Gamma(1+n)}{\Gamma(1+n-\alpha)} x^{n-\alpha}. \tag{1.5} $$

Property 3. Let $x = kz(k > 0)$ and ${}_0^C D_x^\alpha \gamma(x)$ $(p-1 < \alpha \leq p)$ exists, then the following result is true:

$$ {}_0^C D_x^\alpha \gamma(x) = k^{-\alpha} {}_0^C D_z^\alpha \gamma(kz). \tag{1.6} $$

The following are the some properties of Caputo fractional derivative used in the thesis.

1.4.4 Some Properties of Fractional Operators

$$
\begin{aligned}
&{}_a^C D_x^\alpha((x-a)^v) = \begin{cases} 0, & v \in 0,1,2,...,\lceil\alpha\rceil - 1, \\ \frac{\Gamma(1+v)}{\Gamma(1+v-\alpha)}(x-a)^{v-\alpha}, & v \geq \lceil\alpha\rceil, \end{cases} \\
&{}_0 D_x^\alpha A = \frac{Ax^{-\alpha}}{\Gamma(1-\alpha)}, \\
&{}_a^C D_x^\alpha A = 0, \\
&{}_a^C D_x^\alpha(\lambda f(x) + \mu g(x)) = \lambda \left({}_a^C D_x^\alpha f(x)\right) + \mu \left({}_a^C D_x^\alpha g(x)\right).
\end{aligned}
$$

It has been observed that the constant fractional diffusion equation is unable to describe anomalous solute diffusion in complex media because the diffusion behavior varies during the diffusion process when the medium structure changes over time. Therefore, the fractional diffusion equation of variable order is introduced to address such phenomena. The variable-order fractional derivative have the potential to describe various physical situation because of their non-local property, and characterize the memory property of a system. Lorenzo and Hartly [56] discussed some basic features of variable-order operator. These operators can also be drive the self-similarity and hereditary property of a system.

1.4.5 Kronecker Product

Definition: Let two matrices M of order $p_1 \times q_1$ and N of order $p_2 \times q_2$ then the Kronecker product of M and N is denoted by $M \otimes N$, which is a matrix of order

$p_1p_2 \times q_1q_2$ having the following block structure

$$M \otimes N = \begin{pmatrix} m_{1,1}N & m_{1,2}N & \cdots & m_{1,q_1}N \\ m_{2,1}N & m_{2,2}N & \cdots & m_{2,q_1}N \\ \vdots & \vdots & \cdots & \vdots \\ m_{p_1,1}N & m_{p_1,2}N & \cdots & m_{p_1,q_1}N \end{pmatrix} \tag{1.7}$$

where

$$M = \begin{pmatrix} m_{1,1} & m_{1,2} & \cdots & m_{1,q_1} \\ m_{2,1} & m_{2,2} & \cdots & m_{2,q_1} \\ \vdots & \vdots & \cdots & \vdots \\ m_{p_1,1} & m_{p_1,2} & \cdots & m_{p_1,q_1} \end{pmatrix} \qquad N = \begin{pmatrix} n_{1,1} & n_{1,2} & \cdots & n_{1,q_2} \\ n_{2,1} & n_{2,2} & \cdots & n_{2,q_2} \\ \vdots & \vdots & \cdots & \vdots \\ n_{p_2,1} & n_{p_2,2} & \cdots & n_{p_2,q_2} \end{pmatrix}$$

1.5 Some Numerical Methods for Solving Fractional Diffusion Problems

1.5.1 Non-Standard Finite Difference Method (NSFDM)

Standard difference schemes generally preserve the features of the represented system in the form of differential equations when the discretization value is small enough. Mickens [57] presented the idea of non-standard finite difference (NSFD) schemes to understand the phenomenon of numerical instabilities. He then explained the NSFD scheme for various situations in his research publications. As per Mickens, NSFD schemes adhere to five fundamental principles: positivity, periodicity, monotonicity, stability, and other invariants like energy and geometrically defined shapes. The basic definition of NSFD is given in chapter 2 of this thesis. A more accurate and accessible translation of the differential equations is known as an NSFD

model. By building a discrete model, NSFD schemes are a generic collection of approaches in numerical analysis that provide numerical solutions to differential equations. Several excellent contemporary papers have also been published to show the applications of NSFD to the fractional differential equations. Moaddya [58] devised an NSFD methodology to solve linear partial differential equations with fractional derivatives in time and space, and the fractional derivatives were approximated using the Grunwald-Letnikov method.

1.5.2 Spectral Collocation Method

In several engineering and technological domains, the spectral approach has been a dependable choice for acquiring the numerical solutions to the partial differential equations. One broad approximate analytical technique for solving various nonlinear differential equations is the spectral collocation method (SCM).In SCM, first we take a spectral representation of the dependent variable in terms of the polynomial of finite degree. Basically, the spectral representation of the dependent variable is its orthogonal projection of the space of polynomials of finite degree. In the next step, the approximation of the derivatives of the dependent variables are taken in terms of the considered polynomials. After that, the apporixation of dependent variable and its all derivatives are substituted in the given differential equations that produce residual of the differential equations. The constucted residual is then set to zero at different collocation points within the specified domain. This procedure generates system of algebraic equations, and the solution of this system provides an approximation of the problem's solution. Unlike other spectral methods, SCM adopts a strong form of the differential equation directly instead of using a weak form when creating algebraic equations. The collocation method is popular in the engineering technology industry because of its advantages of high speed and precision.

In this thesis, the residual corresponding to the differential equations are construted with the help of Vieta-Fibonacci, Vieta-Lucas and Airfoil polynomials. Here, the derivatives of dependent variables are approximated by the operational matrices of differentiation with the help of above polynomials. After that SCM is applied to find approximate solutions to the different kinds of linear and nonlinear diffusion equations.

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