An Analytical Approach to Pollutant Transport in Unsaturated Porous Media with Adsorption using Nitrates

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***Abstract*—Most investigators use a coordinate change called (z - ut) to solve the equation that describes how pollutants spread in moving fluids through porous materials. They also use boundary conditions like C = 0 at z = □ and C = C_0 at z = -□ for t > 0, which helps create a symmetrical concentration pattern. In this paper, the effect of adsorption using nitrates is studied for one-dimensional movement of pollutants through unsaturated porous materials. The advection-dispersion equation is solved analytically here to understand how pollutants move, taking into account dissipation coefficients and porosity, while also considering how input pollutant concentrations change with time and depth. The solution is found using Laplace transforms, moving coordinates, and Duhamel's theorem, and it is expressed in terms of the complementary error function.**

***Index Terms*—Advection, dispersion, adsorption, Integral transforms, Fick's law, Moving coordinates, Duhamel's theorem**

I. INTRODUCTION:

In recent years, there has been a lot of interest in how substances move through porous materials. Researchers like Scheidegger (1954), deJong (1958), and Day (1956) have created statistical methods to measure concentration patterns and dispersion coefficients. The advection-diffusion equation explains how solutes move through a medium because of both diffusion and convection. This equation is a kind of partial differential equation that is based on the principle of mass conservation and Fick's law. As concerns about environmental damage and air pollution increase, hydrologists, civil engineers, and mathematical modelers are paying more attention to this equation. Analytical and numerical solutions that take initial and boundary conditions into account help understand how contaminants spread through different kinds of mediums, like air, rivers, lakes, and underground water sources. These insights are crucial for developing strategies to reduce damage. This equation also has uses in many other fields, including soil physics, petroleum engineering, chemical engineering, and biological sciences.

In early studies, researchers tried to simplify the advection-diffusion equation in ideal situations by converting it into a diffusion equation by removing the convection terms (Ogata and Banks 1961; Harleman and Rumer 1963; Bear 1972; Guvanasen and Volker 1983; Aral and Liao 1996; Marshal et al 1996) or by introducing another dependent variable (Banks and Ali 1964, Ogata 1970; Lai and Jurinak 1971; Marino 1974 and Al-Niami and Rushton 1977). They did this by using moving coordinates or by introducing another dependent variable. Then the Laplace transformation technique was applied to get the needed solutions.

One-dimensional solutions were created (Tracy 1995) by turning the nonlinear advection-diffusion equation into a linear form, allowing for two-dimensional and three-dimensional solutions. Researchers have proposed methods for solving transport equations for solutes that are absorbed in porous materials with varying velocity fields and dispersion coefficients (Van Kooten 1996, Sudheendra et al. 2014).

Later studies found that some large underground formations show varying dispersivity depending on time or distance (Matheron and deMarsily 1980; Sposito et al. 1986; Gelhar et al. 1992). Analytical solutions were made to show the movement of dissolved substances in complex, semi-infinite porous materials, taking into account distance-dependent dispersion in a constant flow (Yates 1990, 1992). The temporal moment solution for one-dimensional solute transport was used to analyze data from soil column experiments (Pang et al. 2003, Sudheendra et al. 2014). An analytical method was developed for non-equilibrium transport of reactive solutes during water infiltration and redistribution cycles.

Solute movement happens through advection and follows linear kinetics. Solutions were given for solute transport in rivers, including effects like temporary storage and decay (Smedt 2006, Sudheendra 2011, 2012). For groundwater contaminant transport in heterogeneous materials (Sirin 2006), pore flow velocity was treated as a random function of space and time. A semi-analytical solution studied interactions between streams and aquifers in coastal areas, where groundwater levels respond to tides (Kim et al. 2007).

The approach to solving the dispersion process equation is explained more simply here. It is assumed that there is no mass transfer between solid and liquid phases, and that the porous medium is both isotropic and homogeneous. It is also assumed that a planar area is multiplied by a dispersion coefficient, and the concentration gradient is considered. The medium is treated as having a unidirectional model, with average velocity being the same everywhere in the flow field. In this paper, solutions for two problems of solute dispersion in a finite domain are presented. The first problem looks at how solute dispersion changes over time for fully turbulent flow in a polished domain with nitrates. The output condition is constant in nature along with a differential condition.

II. MATHEMATICAL FORMULATION AND MODEL

In the presence of toxic material, the x-z plane with semi-infinite porous media has one-dimensional unsteady flow in the form of a semicircle. However, there is proof that such a discontinuity exists. It is also noted that as long as the medium is isotropic and homogeneous, the assumptions about all physical quantities can still be kept.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - w\frac{\partial C}{\partial z} - \frac{(1-n)}{n}K_d C \tag{1}$$

where C is the constituent concentration in the soil solution, t is the time in minutes, D is the hydrodynamic dispersion coefficient, z is the depth, u is the average pore-water velocity and $\frac{1-n}{n}K_d C$ is the adsorption term.

A fluid with concentration C equal to zero begins to flow initially in the medium. At time t equals zero, the concentration of the plane source is abruptly set to C equal to C0. Subsequently, the initial and boundary conditions (Fig. 1 For a semi-infinite column and for a step input, respectively.

$$\left.\begin{aligned} C(z,\ 0) &= 0\ ; \quad z \geq 0 \\ C\ (0,\ t) &= C_0\ ; \quad t \geq 0 \\ C(\infty,\ t) &= 0\ ; \quad t \geq 0 \end{aligned}\right\} \tag{2}$$

The problem then is to characterize the concentration as a function of x and t.

To reduce equation (1) to a more familiar form, let

$$C(z,\ t) = \Gamma(z,\ t)\exp\left[\frac{wz}{2D} - \frac{w^2 t}{4D} - \frac{(1-n)}{n}K_d t\right] \tag{3}$$

Substitution of equation (3) reduces equation (1) to Fick’s law of diffusion equation

$$\frac{\partial \Gamma}{\partial t} = D\frac{\partial^2 \Gamma}{\partial z^2} \tag{4}$$

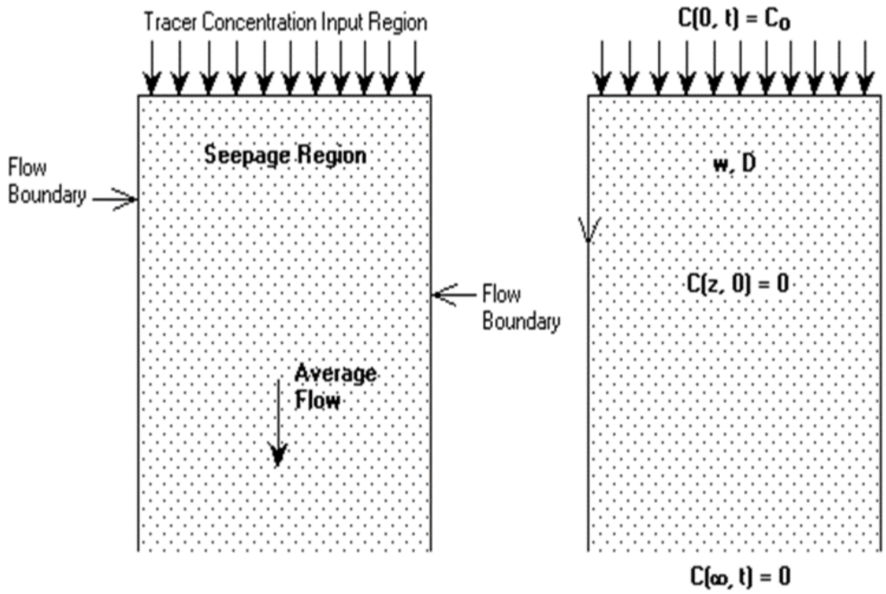

Figure 1 : Physical Layout of the Model

The above initial and boundary conditions (2) transform to

$$\left.\begin{aligned} \Gamma(0,\, t) &= C_0\ \exp\left(\frac{w^2 t}{4D} + \frac{(1-n)}{n} K_d t\right); \quad && t \geq 0 \\ \Gamma(z,\ 0) &= 0\,; && z \geq 0 \\ \Gamma(\infty,\, t) &= 0\,; && t \geq 0 \end{aligned}\right\} \tag{5}$$

Therefore, it is necessary to solve equation (4) for a time-varying fluid influx at z = 0. Equation (4) can be solved employing Duhamel's principle [Carslaw and Jeager, 1947].

Given that phi(t) represents the temperature at the boundary, the solution to the problem where the surface is kept at this temperature phi(t) is identical to the solution for semi-infinite media with zero initial concentration and a surface concentration of unity.

If $C = F(x,\, y,\, z,\, t)$ is the solution of the diffusion equation for semi-infinite media in which the initial concentration is zero and its surface is maintained at concentration unity, then the solution of the problem in which the surface is maintained at temperature $\phi(t)$ is

$$C = \int_0^t \phi(\tau)\,\frac{\partial}{\partial t} F(x, y, z, t-\tau)\; d\tau.$$

This theorem is primarily applied to heat conduction issues, but it has been refined to suit this particular case of concern.

Now consider the scenario where the starting concentration is zero and the boundary concentration remains at one. The parameters governing the limits are

$$\left.\begin{aligned} \Gamma(0,\, t) &= 1\,; \quad && t \geq 0 \\ \Gamma\ (z,\, 0) &= 0\,; && z \geq 0 \\ \Gamma(\infty,\, t) &= 0\,; && t \geq 0 \end{aligned}\right\}.$$

The solution to this issue can be achieved through the use of the Laplace transform. The Γ concentration, which depends on time t and spatial coordinates z, x, y, occurs within the problem. We compose

$$\overline{\Gamma}(z,\ p) = \int_0^\infty e^{-pt}\ \Gamma(z,\, t)\, dt$$

Hence, if equation (4) is multiplied by e^{-pt} and integrated term by term it is reduced to an ordinary differential equation

$$\frac{d^2\overline{\Gamma}}{dz^2} = \frac{p}{D}\,\overline{\Gamma} \tag{6}$$

The solution of the equation (6) can be written as

$$\overline{\Gamma} = A\,e^{-qz} + B\,e^{qz}$$

where $q = \sqrt{\dfrac{p}{D}}$.

The boundary condition as z → ∞ requires that B = 0 and boundary condition at z = 0 requires that $A = 1/p$, thus the particular solution of the Laplace transform equation is

$$\overline{\Gamma} = \frac{1}{p}\,e^{-qz}$$

The inversion of the above function is given in a table of Laplace transforms (Carslaw and Jaeger, 1947). The result is

$$\Gamma = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right) = \frac{2}{\sqrt{\pi}} \int_{\frac{z}{2\sqrt{Dt}}}^{\infty} e^{-\eta^2}\,d\eta. \tag{7}$$

Applying Duhamel's principle, the solution to the problem with an initial concentration of zero and a time-varying surface condition at z = 0 is.

$$\Gamma = \int_0^t \phi(\tau)\,\frac{\partial}{\partial t}\left[\frac{2}{\sqrt{\pi}} \int_{\frac{z}{2\sqrt{Dt}}}^{\infty} e^{-\eta^2}\,d\eta\right] d\tau$$

since $e^{-\eta^2}$ is a continuous function, it is possible differentiate under the integral, which gives

$$\frac{2}{\sqrt{\pi}}\frac{\partial}{\partial t} \int_{\frac{z}{2\sqrt{D(t-\tau)}}}^{\infty} e^{-\eta^2}\,d\eta = \frac{z}{2\sqrt{\pi D}(t-\tau)^{3/2}}\, e^{-z^2/4D(t-\tau)}$$

The solution of the problems is

$$\Gamma = \frac{z}{\pi\sqrt{D}} \int_0^t \phi(t)\,e^{-z^2/4D(t-\tau)}\,\frac{d\tau}{(t-\tau)^{3/2}}$$

Letting

$$\mu = \frac{z}{2\sqrt{D(t-\tau)}}$$

the solution can be written as

$$\Gamma = \frac{2}{\sqrt{\pi}} \int_{\frac{z}{2\sqrt{Dt}}}^{\infty} \phi\left(t - \frac{z^2}{4D\mu^2}\right) e^{-\mu^2}\,d\mu.. \tag{8}$$

Since $\phi(t) = C_0 \exp\left(\dfrac{w^2 t}{4D} + \dfrac{(1-n)}{n} K_d t\right)$ the particular solution of the problem can be written as

$$\Gamma(z,t) = \frac{2C_0}{\sqrt{\pi}}\, e^{\left(\frac{w^2}{4D} + \frac{(1-n)}{n}K_d\right)t} \left\{\int_0^{\infty} \exp\left(-\mu^2 - \frac{\varepsilon^2}{\mu^2}\right) d\mu - \int_0^{\alpha} \exp\left(-\mu^2 - \frac{\varepsilon^2}{\mu^2}\right) d\mu\right\} \tag{9}$$

where $\varepsilon = \sqrt{\left(\dfrac{w^2}{4D} + \dfrac{(1-n)}{n}K_d\right)}\,\dfrac{z}{2\sqrt{D}}$ and $\alpha = \dfrac{z}{2\sqrt{Dt}}$.

III. EVALUATION OF THE INTEGRAL SOLUTION

The integration of the first term of equation (9) gives (Pierce, 1956)

$$\int_0^{\infty} e^{-\mu^2 - \frac{\varepsilon^2}{\mu^2}}\, d\,\frac{(1-n)}{n} K_d C = \frac{\sqrt{\pi}}{2}\, e^{-2\varepsilon}$$

Conveniently, the second integral can be represented using the error function (Horenstein, 1945), as this function is readily available in tables. Observing that

$$-\mu^2 - \frac{\varepsilon^2}{\mu^2} = -\left(\mu + \frac{\varepsilon}{\mu}\right)^2 + 2\varepsilon$$

$$= -\left(\mu - \frac{\varepsilon}{\mu}\right)^2 - 2\varepsilon$$

The second integral of equation (9) can be written as

$$I = \int_0^\alpha \exp\left(-\mu^2 - \frac{\varepsilon^2}{\mu^2}\right) d\mu \; = \frac{1}{2}\left\{ e^{2\varepsilon} \int_0^\alpha \exp\left[-\left(\mu + \frac{\varepsilon}{\mu}\right)^2\right] d\mu + e^{-2\varepsilon} \int_0^\alpha \exp\left[-\left(\mu - \frac{\varepsilon}{\mu}\right)^2\right] d\mu \right\} \tag{10}$$

Because the technique of converting integrals into tabulated functions is identical for both integrals on the right side of equation (10), only the first term is taken into account. Let $a = \frac{\varepsilon}{\mu}$ and adding and subtracting, we get

$$e^{2\varepsilon} \int_{\varepsilon/\alpha}^{\infty} \exp\left[-\left(a + \frac{\varepsilon}{a}\right)^2\right] da .$$

The integral can be expressed as

$$I = e^{2\varepsilon} \int_0^\alpha \exp\left[-\left(\mu + \frac{\varepsilon}{\mu}\right)^2\right] d\mu = -e^{2\varepsilon} \int_{\varepsilon/\alpha}^{\infty} \left(1 - \frac{\varepsilon}{a^2}\right) \cdot \exp\left[-\left(\frac{\varepsilon}{a} + a\right)^2\right] da + e^{2\varepsilon} \int_{\varepsilon/\alpha}^{\infty} \exp\left[-\left(\frac{\varepsilon}{a} + a\right)^2\right] da .$$

Further, let

$$\beta = \left(\frac{\varepsilon}{a} + a\right)$$

in the first term of the above equation, then

$$I_1 = -e^{2\varepsilon} \int_{\alpha + \frac{\varepsilon}{\alpha}}^{\infty} e^{-\beta^2} d\beta + e^{2\varepsilon} \int_{\varepsilon/\alpha}^{\infty} \exp\left[-\left(\frac{\varepsilon}{a} + a\right)^2\right] da .$$

Similar evaluation of the second integral of equation (10) gives

$$I_2 = e^{-2\varepsilon} \int_{\varepsilon/\alpha}^{\infty} \exp\left[-\left(\frac{\varepsilon}{a} - a\right)^2\right] da - e^{-2\varepsilon} \int_{\varepsilon/\alpha}^{\infty} \exp\left[-\left(\frac{\varepsilon}{a} - a\right)^2\right] da$$

Again substituting $-\beta = \frac{\varepsilon}{a} - a$ into the first term, the result is

$$I_2 = e^{-2\varepsilon} \int_{\frac{\varepsilon}{\alpha} - \alpha}^{\infty} e^{-\beta^2} d\beta - e^{-2\varepsilon} \int_{\varepsilon/\alpha}^{\infty} \exp\left[-\left(\frac{\varepsilon}{a} - a\right)^2\right] da .$$

Noting that

$$\int_{\varepsilon/\alpha}^{\infty} \exp\left[-\left(a + \frac{\varepsilon}{a}\right)^2 + 2\varepsilon\right] da = \int_{\varepsilon/\alpha}^{\infty} \exp\left[-\left(\frac{\varepsilon}{a} - a\right)^2 - 2\varepsilon\right] da$$

Substitute this into equation (10) gives

$$I = e^{-2\varepsilon} \int_{\frac{\varepsilon}{\alpha}-\alpha}^{\infty} e^{-\beta^2} d\beta - e^{2\varepsilon} \int_{\frac{\varepsilon}{\alpha}+\alpha}^{\infty} e^{-\beta^2} d\beta .$$

Thus, equation (9) can be expressed as

$$\Gamma(z,t) = \frac{2C_0}{\sqrt{\pi}} e^{\left(\frac{w^2}{4D}+\frac{(1-n)}{n}K_d\right)t} \cdot \left\{ \frac{\sqrt{\pi}}{2} e^{-2\varepsilon} - \frac{1}{2}\left[e^{-2\varepsilon} \int_{\frac{\varepsilon}{\alpha}-\alpha}^{\infty} e^{-\beta^2} d\beta - e^{2\varepsilon} \int_{\frac{\varepsilon}{\alpha}+\alpha}^{\infty} e^{-\beta^2} d\beta \right] \right\} \quad (11)$$

However, by definition

$$e^{2\varepsilon} \int_{\alpha+\frac{\varepsilon}{\alpha}}^{\infty} e^{-\beta^2} d\beta = \frac{\sqrt{\pi}}{2} e^{2\varepsilon} erfc\left(\alpha + \frac{\varepsilon}{\alpha}\right)$$

also,

$$e^{-2\varepsilon} \int_{\frac{\varepsilon}{\alpha}-\alpha}^{\infty} e^{-\beta^2} d\beta = \frac{\sqrt{\pi}}{2} e^{-2\varepsilon} \left[1 + erf\left(\alpha - \frac{\varepsilon}{\alpha}\right) \right]$$

Writing equation (11) in terms of the error functions, we get

$$\Gamma(z,t) = \frac{C_0}{2} e^{\left(\frac{w^2}{4D}+\frac{(1-n)}{n}K_d\right)t} \left[e^{2\varepsilon} erfc\left(\alpha + \frac{\varepsilon}{\alpha}\right) + e^{-2\varepsilon} erfc\left(\alpha - \frac{\varepsilon}{\alpha}\right) \right]$$

Substitute the value of $\Gamma(z,t)$ in equation (3) the solution reduces to

$$\frac{C}{C_0} = \frac{1}{2} \exp\left[\frac{wz}{2D}\right] \left[e^{2\varepsilon} erfc\left(\alpha + \frac{\varepsilon}{\alpha}\right) + e^{-2\varepsilon} erfc\left(\alpha - \frac{\varepsilon}{\alpha}\right) \right]. \quad (12)$$

Resubstituting the value of ε and α gives

$$\frac{C}{C_0} = \frac{1}{2} \exp\left[\frac{wz}{2D}\right] \left[\exp\left[\left(\sqrt{\frac{w^2}{4D} + \frac{(1-n)}{n} K_d} \right) \frac{z}{\sqrt{D}} \right] \cdot erfc\left(\frac{z}{2\sqrt{Dt}} - \sqrt{\frac{w^2 t}{4D} + \frac{(1-n)}{n} K_d t} \right) \right.$$

$$\left. + \exp\left[-\left(\sqrt{\frac{w^2}{4D} + \frac{(1-n)}{n} K_d} \right) \frac{z}{\sqrt{D}} \right] \right]. \quad \cdot erfc\left(\frac{z}{2\sqrt{Dt}} - \sqrt{\frac{w^2 t}{4D} + \frac{(1-n)}{n} K_d t} \right) \quad (13)$$

In cases where boundaries are symmetrical, the solution to the problem is found using the first term of equation (13). The second term in equation (13) comes from the asymmetric boundary conditions in a general problem. However, it should be noted that when considering a point far from the source, the boundary conditions can be approximated as $C(-\infty, t) = C_0$, leading to a symmetrical solution.

IV. RESULTS & DISCUSSIONS:

The analytical methods have some important limits. They work best when the problems are not too complicated and when the shape of the area being studied is regular. The soil must be the same in all parts of the area being studied. Compared to other methods for solving one-dimensional transport models, the analytical approach is a bit more flexible. Figures 1 to 4 show how the concentration of a substance changes as it moves through different parts of the media, depending on the amount of empty space (porosity). When the speed of fluid flow, the spread of the substance (dispersion), and the way it sticks to the soil (distribution coefficient K_d) are constant, the ratio of current concentration to original concentration (C/C0) decreases as the depth increases, especially when porosity is lower. When you look at how concentration changes over time at different depths, it starts to increase because the spread effect (dispersion coefficient K_d) has less impact. Eventually, it reaches a steady level after a longer period of time.

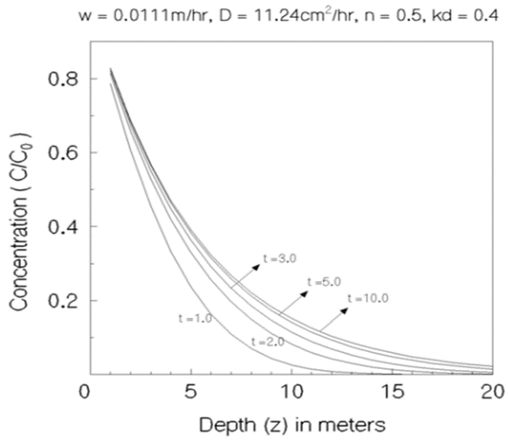

Fig. 1: Break-through-curve for C/C_0 v/s depth for n=0.5 and K_d=0.4

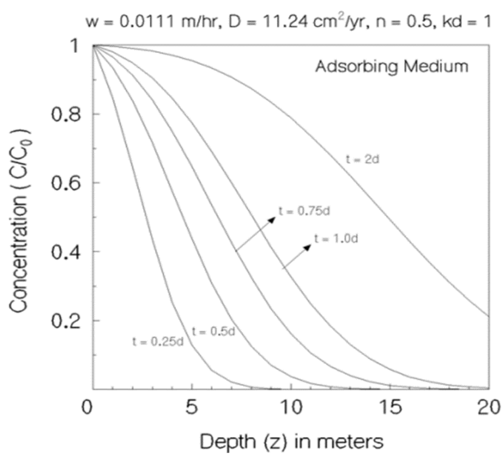

Fig. 2: Break-through-curve for C/C_0 v/s depth for n=0.5 and K_d=1.0

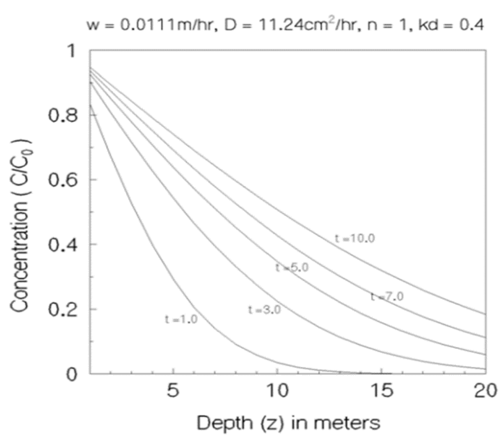

Fig. 3: Break-through-curve for C/C_0 v/s depth for n=1.0 and K_d=0.4

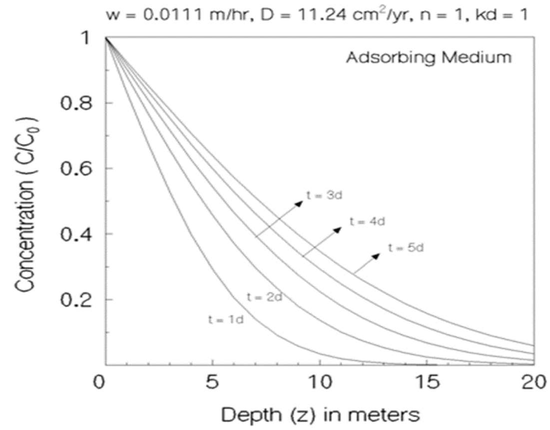

Fig. 4: Break-through-curve for C/C_0 v/s depth for n=1.0 and K_d=1.0

The data shows how C/C0 relates to time for different values of the distribution coefficient K_d. When K_d is fixed, the concentration rises slowly for the first 10 days because the substance isn't easily sticking to the solid parts of the soil. After that, the concentration stays at a constant level, where K_d doesn't matter anymore. The integral transform method is good for solving analytical solutions that involve how a substance moves and how it sticks to materials in uniform porous areas, under various flow conditions. These solutions can be used to directly calculate how concentrations stay the same over time and how concentrations change over time. For situations where things change over time, numerical inversions can be used. These solutions are useful for testing numerical models that simulate how pollutants move and react in the environment.

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