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Mathematical Modelling of Bioremediation of Benzene Contaminated Soil by Biopile Method

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Abstract: The application of numerical methods to solve pollutant transport issues has become popular because of the increased importance of soil-water quality. The current study proposes a two-dimensional numerical model for the bioremediation of benzene from benzene-contaminated soil. Biopile is a technique wherein the contaminated soil is remediated through the process of biodegradation. The model used in the current study simulates Benzene's flow, transport, and biodegradation during the biopile process in saturated porous media using the Finite Difference Method. Provisions were made for the entry and exit of gases or liquids from the pile at specified positions along the bottom liner or pile centreline. The midline for the pile was employed to provide symmetry to lessen the overall complexity of the problem. The double Monod kinetic equation was used to model the bacterial growth within the biopile, whereas the fertilizer transport through soil and movement of fluids inside the soil was modelled using Advection Dispersion Equation (ADE) and Navier-Stokes' equation. The results indicated that the amount of benzene eliminated through outflows was higher for air velocity of 5 m/s compared to air velocity of 1m/s.

Keywords: Benzene Contamination; Biopile; Bioremediation; Transport; Modelling.

1 Introduction

Leaks and spillage of fuels or chemicals from underground storage tanks into the soil, and eventual movement into underground water, are significant causes of organic contamination. Fuel spillage can happen due to process equipment failure or mishandling, and other mishaps [1,2]. Globally the governments have spent billions of dollars over the last few decades trying to clean up areas that have been degraded in this manner

[3]. The environment can recover and purify itself. However, the up to cater on the ecosystem in recent times by massive amounts of industrial pollution has outstripped its ability to recover, necessitating the need to save the environment [4]. Environmental clean-up has always relied on traditional methods [5] and there are many methods being developed for soil remediation [6]. However, bioremediation has lately become a necessity because of its proven environmentally friendly nature [7, 8, 9]. Natural bioremediation, or passive bioremediation, is based on the fact that microbes are abundant in nature and will decompose organic matter at a specific rate, even when it is slow [10]. Because natural processes are so variable, the wealth of literature suggests that bioremediation ability should be assessed using a model, and mathematical transport modelling can help with this [8]. Earlier researchers have modelled bioremediation of polluted soil [8,10-17] but studies pertaining to bioremediation of benzene modelling are scanty. In lieu of this, a brief attempt has been made to describe the ability of naturally existing microbes to decrease pollutants in soil aggregates has been undertaken.

The current analysis aims to assist remediation specialists in recognizing and benefiting from the possible benefits of ex-situ soil pile remediation. A two-dimensional framework of multicomponent transfer, possible mass transfer limits, and biodegradation aspects are provided in this study.

2 Description of Model

The application of an ex-situ method requires contaminated soil to be removed from its initial position and treated above ground. Even though the excavation procedure is costly, there are some advantages to using an ex-situ solution. The development of an encapsulated soil pile keeps polluted soil contained and allows for controlling any releases that occur during treatment.

The current work proposes a remediation assessment framework that allows users to evaluate bioremediation deployed ex-situ to a polluted soil pile. The concept is based on a polluted soil pile dug from its original spot, placed at the top of a bottom liner system, and subsequently enclosed with a cover liner. The liner systems will retain and confine the soil while allowing the controlled entry and exit of fluid movements. The polluted soil can be bio-remediated, utilizing one of many biological functions after the pile has been formed and enclosed. For simulating aeration and fertilizer transport within the soil pile, the equations used are the oxygen diffusion and dispersion equation, and the advection-dispersion equation. The oxygen and fertilizer will be utilized by microorganisms for their growth, and these microorganisms will degrade the benzene. The modeling of benzene biodegradation in the soil pile is done by the Monod equation. The soil-pile concept is depicted schematically in Fig. 1.

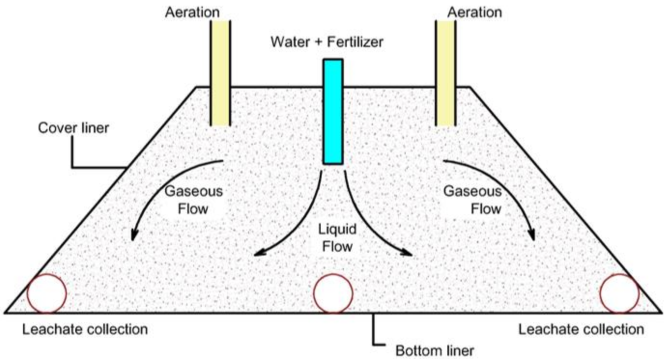

Fig. 1. Typical cross-section of a biopile

2.1 Assumptions made

- Soil is homogenous & saturated.
- The uniform accumulation of contaminants on soil aggregates.
- The presence of microorganisms in the pore fluids and on solid surfaces as microcolonies.
- The growth of microorganisms is by ingesting organic pollutants and oxygen, and water and airflow together through a Biopile.
- Only 2-Dimension taken into account.
- Biodegradation, water, and fertilizer transport occur in the liquid phase only.

2.2 Benzene

Benzene (C_6H_6) shown in Fig. 2 is a natural aromatic hydrocarbon and a source of many important aromatic chemicals. Benzene is among the top 25 priority pollutants at waste disposal sites in North America and Europe. The component, which is highly soluble and is considered toxic in people, is most likely Benzene from the perspective of public health concern. Exposure to Benzene can cause leukemia. In comparison to other mono-aromatic hydrocarbons like toluene (1 g/l) and xylenes (10 g/l), the criterion for Benzene in drinking water is significantly stricter (0.005 g/l), and its presence frequently serves as the impetus for bioremediation of petroleum hydrocarbon locations.

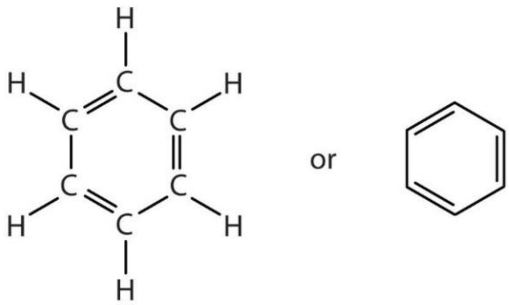

Fig. 2. Structure of benzene molecule

While mono-aromatic hydrocarbons like Benzene, toluene, ethylbenzene, and xylenes (referred to as BTEX) appear to be relatively soluble and are transmitted over greater distances, short-chain alkanes tend to be volatile and are easily removed from soil and groundwater. Under aerobic circumstances, Benzene degrades to CO_2 as shown in Equations 1, 2, and 3.

$$C_6H_6 + 7.5\,O_2 \rightarrow 6\,CO_2 + 3\,H_2O \quad (1)$$

$$\Delta G° = -(30\,e^{-}/\text{mol})\,(96.63\,\text{kJ/V})\,(+0.82 - (-0.29)\,\text{V}) \quad (2)$$

$$\Delta G° = -3{,}200\,\text{kJ/mol or} - 107\,\text{kJ/e} - \text{ equiv transferred (highly feasible)} \quad (3)$$

2.3 Biodegradation

The concentration of hydrocarbons with time has been well described by the double Monod equation (Equation 4):

$$\frac{S\,X}{\frac{\partial S}{\partial t}} = \left(\frac{K_S}{k}\right) + \left(\frac{S}{k}\right) \quad (4)$$

where, S = Substrate concentration (mg-substrate/1); $\frac{\partial S}{\partial t}$ = Substrate utilization rate at (mg-substrate/l. day); X = Microbial concentration (mg-cells/1); k = Maximum specific substrate utilization rate (g-substrate/g-cells/day); and K_s = Half-saturation coefficient (mg-substrate/1).

2.4 Aeration

Considering the oxygen diffusion and dispersion from the air introduced in water mass, the main phenomenon equation (Equation 5) will be as follows:

$$\frac{\partial \bar{C}}{\partial t} + \frac{\partial}{\partial x}(\bar{\mu}\bar{C}) + \frac{\partial}{\partial y}(v\bar{C}) = \frac{\partial}{\partial x}\left(\varepsilon_x \frac{\partial \bar{C}}{\partial t}\right) + \frac{\partial}{\partial y}\left(\varepsilon_y \frac{\partial \bar{C}}{\partial t}\right) + D_m\left(\frac{\partial^2 \bar{C}}{\partial x^2} + \frac{\partial^2 \bar{C}}{\partial y^2}\right) + R(x,y,t) \quad (5)$$

Where, x, y - coordinates of the considered point from the biopile; $C(x,y,t)$ - the concentration of oxygen from the aqueous Medium; D_m – oxygen diffusion constant from air to water, its values depending on temperature (D_m= 0.203 m^2/s at 200C; D_m = 0.155 m^2/s at 100C and D_m = 0.18 m^2/s at 150C); ε_x, ε_y - coefficients of longitudinal and vertical dispersion on the fluid flow; u, v - components of the speed vector and $R(x,y,t)$ - oxygen source or demand in biochemical reactions.

2.5 Fertilizer transport

Understanding the mechanisms of mass transfer from the solid adsorption phase to the liquid phase and pollutant degradation is critical for contamination transport modelling [18, 19]. The exchange of energy in fluids, movement through porous media, and the dispersion of pollutants in fluids, as well as chemical extraction methods, are all examples of advection-dispersion phenomena [20]. The following presumptions form the foundation of the advection-dispersion equation (ADE), which models solute transport in saturated porous media under steady-state flow conditions:

- Fick's law governs the diffusion of solutes in porous media.
- The mass conservation concept in its broadest sense.
- Isotherms of linear sorption.
- The solute flux is influenced by geochemical reactions (sorption).
- In porous media, the solute's pore water velocity is constant.
- Diffusivity coefficients are not affected by the x-axis position.

In the present study, a one-dimensional advection-dispersion equation is considered. The equation depicts how solutes move through a homogeneous soil matrix in a transitional manner. Using the finite element method (FEM), the governing transport equation [21] is shown in Equation 6:

$$R\,\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2} - V\,\frac{\partial C}{\partial x} - \lambda C \quad (6)$$

3 Mathematical Modelling

Defining the pile shape is the initial stage in modelling a soil pile restoration. Fig. 3 shows the model is established on a simplified geometry, which depicts a trapezoidal enclosed pile of soil placed astride a liner system. In the third dimension, it is assumed that this portion remains constant. Everything apart from heat energy is thought to pass through the cover liner system. The base liner is presumed to be permeable to fluids like water and gas at the locations provided by the user. Because this application necessitates encapsulation, mechanisms have been created to infuse or extract fluids in or out of the pile at user-specified positions towards the base liner or the pile midline.

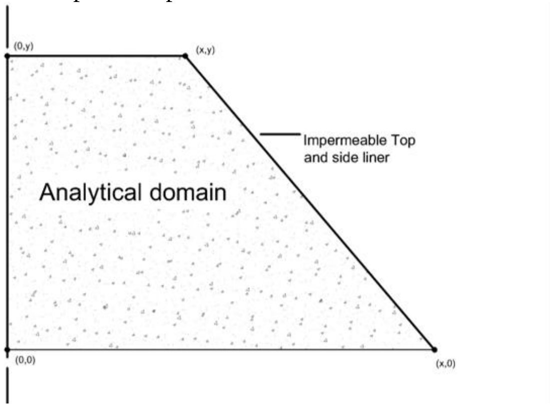

Fig. 3. Analytical domain for ex-situ soil pile

Fig.1 geometry is transformed into an analytical state area in Fig. 3. After defining the soil pile design, the next stage in the ex-situ remediation process is to develop a flow field model to study fluid fluxes through the pile. Various fluid units were developed for these geometries, depending on the region's saturation, whether the flow is continuous or transient, and how much physical/chemical interactions modify the soil's hydraulic properties.

4 Methods of Solution

The two coefficients that describe Monod's empirical expression are unique to a specific system. Therefore, it is essential to use caution when extending coefficients found in one setting to another. Lawrence and McCarty [22] adapted Monod's (1949) hyperbolic equation [23] to reflect the influence of substrate concentration on the rate at which microbes eliminate limiting substrates. The intrinsic coefficients k and K_s define Monod's equation. Because of its simplicity, acceptable data were spreading, and accuracy of least-square fit, the Hanes function was chosen in the current study [24, 25]. Monod's equation is linearized via a double inversion followed by S multiplication to obtain Equation 7:

$$\frac{S\,X}{\frac{\partial S}{\partial t}} = \left(\frac{K_S}{k}\right) + \left(\frac{S}{k}\right) \tag{7}$$

where, S = Substrate concentration (mg-substrate/1); $\frac{\partial S}{\partial t}$ = Substrate utilization rate at (mg-substrate/l. day); X = Microbial concentration (mg-cells/1); k = Maximum specific substrate utilization rate (g-substrate/g-cells/day); and K_s = Half-saturation coefficient (mg-substrate/1).

Water and air are assumed insoluble. The pile is assumed to be homogenous, with symmetric flows perpendicular and parallel to the extraction pipes at the bottom of the pile. The construction method is inherently conducive to producing a nearly uniform pile. Equation 8 is a simplification that is comparable to assuming a constant air density in terms of mathematics.

$$k_{r,a}\left[\frac{\partial^2 P_a}{\partial x^2}+\frac{\partial^2 P_a}{\partial y^2}+\frac{\partial^2 P_a}{\partial z^2}\right]+\frac{\partial P_a}{\partial x}\left(\frac{\partial k_{r,a}}{\partial x}\right)+\frac{\partial P_a}{\partial y}\left(\frac{\partial k_{r,a}}{\partial y}\right)+\frac{\partial P_a}{\partial z}\left(\frac{\partial k_{r,a}}{\partial z}\right)=0 \qquad (8)$$

Relative pressures can be employed in the computations if the higher degree terms are removed, in turn reducing the need to manipulate differences between big values. As a result, the computation time is reduced, and the accuracy is greatly improved.

This step has two conservation equations and four unknowns: P_a, P_w, $k_{r,w}$ and $k_{r,a}$. Fluid surface tension, a function of pore shape and the relative amounts of water and air in the pore, causes the local differential between pore water and pore air pressure [26]. After that, for a specific media, Equation 9 is considered.

$$P_a - P_w \equiv P_c = f_1(S_w, S_a) \qquad (9)$$

The exit border conditions are specified for the bottom of biopile where the leachate collection system is installed. The exit border condition is established using a trial and error method. In this area, the soil is usually relatively close to saturation. Mass flows into and out of the pile are computed and compared based on this principle. The computations stop if both air and water are conserved; if not, the interface saturation, $S_{w,grav}$, is reduced, and the sequence continues. The water boundary conditions are defined mathematically (Equations 10 & 11) as:

$$S_w = S_{w,sat} \ @\ pile\ surfaces \qquad (10)$$

$$S_w = S_{w,grav} \ @\ bottom\ of\ gravel\ bed \qquad (11)$$

where n = direction normal to the surface of interest and

mw = mass flux of water sprayed on the pile

The boundary conditions governing the air flow through the pile are straightforward (Equations 12, 13 & 14):

$$P_a = P_{ambient} \ @\ pile\ surfaces \qquad (12)$$

$$\frac{\partial P}{\partial n} = 0 \ @\ bottom\ and\ surface\ of\ symmetry \qquad (13)$$

$$P_a = P_{b,lower} \ @\ gravel\ bed \qquad (14)$$

A 2D model has been developed to describe water and fertilizer motion in saturated porous media, which was used to resolve the Richards problem for saturated porous media using the finite element approach, resulting in broad expressions for starting and boundary conditions as well as water and fertilizer transport. All water-solute flow in porous media is governed by the conservation of matter rule (soil). Because of advection (induced by water movement), dispersion (resulting from mechanical mixing), and molecular diffusion, a fertilizer injected into soil-water spreads out and travels with it. Equation 15 represents the one-dimensional representation of the fertilizer transfer in soil-water:

$$D_L \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} = T \frac{\partial y}{\partial t} \quad (15)$$

where C represents fertilizer concentration, V represents the seepage pore water velocity on average, D_L is the coefficient of longitudinal dispersion and T represents the retardation factor.

The Finite difference method is a group of numerical approaches for estimating derivatives with finite differences to solve ordinary and partial differential equations. The solution's value at these discrete points is approximated by solving algebraic equations, including finite differences and values from neighboring points, and both the geographic domain and time interval are discretized or divided into a finite number of steps (Equations 16, 17, & 18). Forward Time Centered Space applied to diffusion problem using forward difference at time tn and a second order central difference for the space derivative at location x:

$$\frac{\partial u}{\partial t} = \propto \frac{\partial^2 u}{\partial x^2} \quad (16)$$

The FTCS scheme is as follows:

$$\frac{u_i{}^{n+1} - u_i{}^n}{\Delta t} = \frac{\propto}{\Delta x^2} (u_{i+1}{}^n - 2u_i{}^n + u_{i-1}{}^n) \quad (17)$$

By letting $r = \frac{\propto \Delta t}{\Delta x^2}$, we get,

$$u_i{}^{n+1} = u_i{}^n + r (u_{i+1}{}^n - 2u_i{}^n + u_{i-1}{}^n) \quad (18)$$

The explicit finite difference approach is used to solve the equations analytically, and the results are programmed in MATLAB.

5 Results and discussion

At concentrations less than 0.1 g/1, Monod's equation adequately represented the biodegradation rates of Benzene. The applicability of Monod's equation was supported by the high correlation coefficients (r=0.991 for Benzene) found by the Hanes linearization. However, a linearization technique's correlation is insufficient evidence for proving proper Monod fit. For Benzene, the estimated Monod coefficients were utilized to compare simulated vs observed specific substrate consumption rates as a function of substrate concentration, and the satisfactory fit of Monod's equation to the kinetics data was demonstrated.

Different operating circumstances yielded different results. Aeration method variation, a key functional parameter, resulted in a wide range of pollutant dispersion and fluid flow patterns within a biopile. However, the air flow dynamics of the environment were similar for all aeration/non-aeration methods. Fig. 5 depicts a typical fluid flow of such scenarios with an input airspeed of 1m/s. Regardless of the inflow velocity, which ranged from 1 to 5 m/s, the general flow patterns remained the same.

Non-aerated and perpendicular aeration pipe instances illustrate that a higher air speed can result in slightly increased pollutant loss to the atmosphere. However, because the benzene in the 5 m/s instance is more than in the 1 m/s example, as in Fig. 6 the benzene concentration decrease may be greater. As a result, even when biodegradation is considered, the overall benzene removal potential of biopile surface loss to the atmosphere for 5 m/s airspeeds is still higher than that for 1 m/s airspeed.

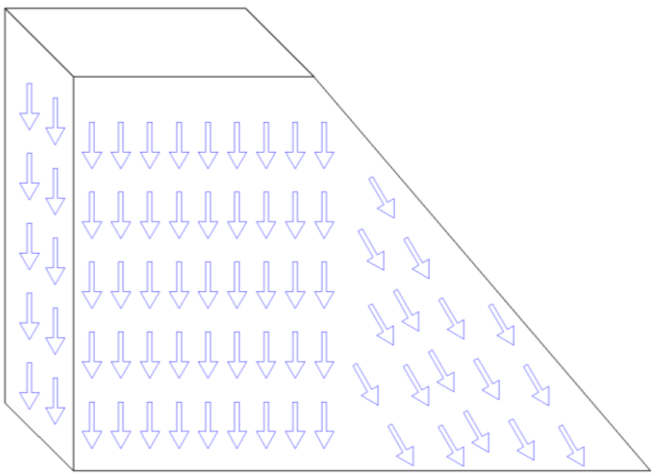

Fig. 5. Air flow pattern in a biopile system

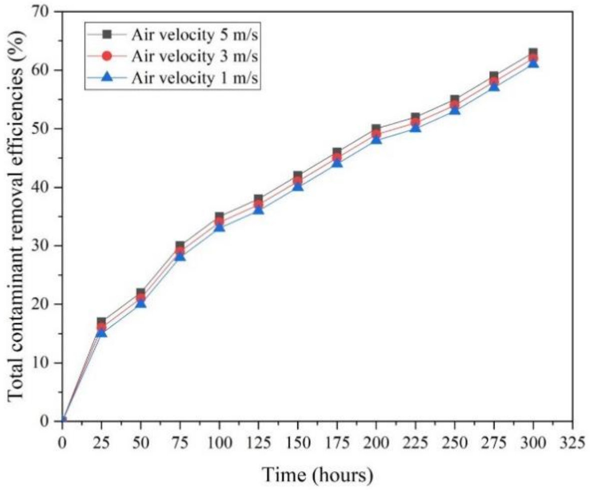

Fig. 6. Variation in benzene removal efficiencies with air velocities

The aerobic biodegradation of organic pollutants requires oxygen, the preferred electron acceptor. Typically, the air is injected or extracted from the pile using pipes to provide oxygen. The concentration of fertilizer against time with different oxygen diffusion coefficients are depicted in Fig. 7. For pile performance, the aeration rate is regarded as the most crucial element in composting systems.

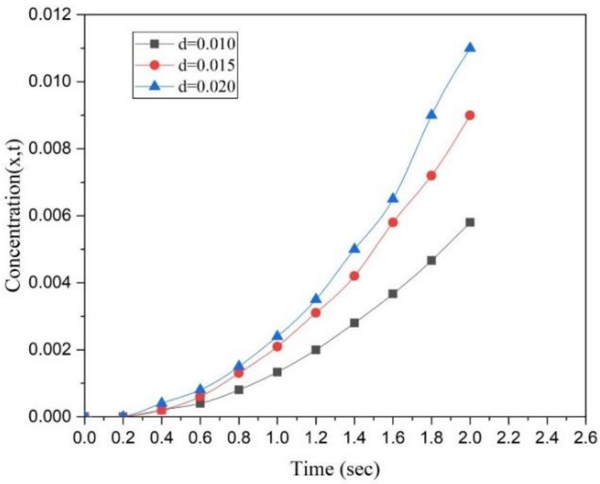

Fig. 7. Concentration of fertilizer against time with different oxygen diffusion coefficient

6 Conclusions

An examination of benzene bioremediation performed on an ex-situ dirt pile is presented using a model. The proposed model can mimic nutritional stimulation and toxic inhibition of organics, with fundamentally distinct aerobic and anaerobic bioremediation possibilities. The governing mass transport equations are numerically solved using a finite difference approximation method. The following conclusions are drawn from the study:

- The modelling study revealed that aqueous quantities of Benzene greater than 0.1g/l were inhibitory, and Monod's equation was ineffective at such high concentrations.
- Mathematical model equations were employed to describe the fertilizer and soil water movement, concentrations. The results show that as the simulation time grows, the fertilizer concentration also increases.
- The modelling studies indicated that as the air velocity increased, the amount of benzene eliminated through outflows to the environment through the pile surfaces also increased. Additionally, the aerated biopile with velocity 5 m/s yielded higher benzene removal compared to lower velocity of 1 m/s.

Furthermore, the approach developed from the present study governing mathematical equations and solved using MATLAB can be inferred to be a novel tool to analyze the performance of a biopile with regards to the surrounding environmental conditions for the case of benzene. This approach can broaden the scope of the research object to include most of the environmental impacts, such as the usage of energy and the environmental footprint in addition to other contaminant removals.

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