Bioremediation Process for Oil Contaminated Underground Water

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Abstract. The petroleum crude is a pollutant that penetrates from surface soils and reaches to the underground water sources. An experimental setup was used for validating bioremediation method that prevents pollutant dispersion in the underground water sources. For this purpose, diluted Autotrophicus bacterium the water was injected into a reservoir and recovered from a well at downstream. Furthermore, a numerical model based on diffusion of the pollutant in the porous media and a disappearing reaction rate was used for validation of existing models in proposed method. Finally, experimental and model results show that injection rate of microorganism has an optimum. In present work, bioremediation process in the experimental setup that has a recycling pattern was introduced for tracing of contaminant dispersion, and the results of a numerical modeling was validated versus experiment data. Moreover, biodegradation reaction cause to reduction of pollutant dispersion flux that shows better microorganism performance in the aquifer.

1. Introduction
Groundwater contamination is considered to be one of the most significant ecological and health problems, and it greatly affects the general environmental features of large regions and drinking water supply conditions in many countries [1]. The protection of public water supplies is of paramount importance. Groundwater, the main source of drinking water for about 50% of the world's total population, is said to be contaminated if some hazardous compounds in the water meet or exceed U.S. EPA standards [2].

The several research studies have been done for providing valuable experimental data in places that possibility of underground contamination exists. These studies help to taking strategies for preventing or controlling of pollutant distribution. For example, Liu et al. and Al-Awadi et al. reported field data of different places, otherwise, Lucianoa et al. and Ayotamuno et al. reported laboratory data [3-6].

Hes et al. studied bioremediation of a diesel fuel contaminated aquifer in laboratory aquifer [7]. Likewise Chen et al. [8], with application of enhanced bioremediation system from the spill area to the down gradient area (located approximately 300 m from the source area) found that the percentage of total hydrocarbon removal increased [9].

Contaminants can adhere to soil and subsequent rainfall can leach the adhered contaminant into groundwater. Recently, Clinton et al., Mirbagheri and Hashemi Monfared, and Du and Liang reported that state using numerical modeling has benefits and it could be used for anticipating of contaminant transportation in the porous media [10-12]. In addition, Suarez and Rifai studied about kinetic model of bioremediation and reported reaction rate parameters for several in situ cases [13].
2. Modeling

2.1. Flow in variably saturated porous media

Richards’ equation models flow in variably saturated porous media. With variably saturated flow, hydraulic properties change as fluids move through the medium, filling some pores and draining others.

\[
\left( \frac{c}{\rho g} + s_e \right) \frac{\partial p}{\partial t} + \nabla \cdot \left[ -k_s \mu k_r \nabla (p + \rho gh) \right] = Q_s
\]

where pressure, \(p\), is the dependent variable. \(C\) represents the specific capacity, \(Se\) denotes the effective saturation, \(S\) is the storage coefficient, \(K_s\) gives the hydraulic permeability, \(\mu\) is the fluid dynamic viscosity, \(k\) denotes the relative permeability, \(p\) is the fluid density, \(g\) is acceleration of gravity, \(h\) represents the vertical coordinate, and \(Q_s\) is the fluid source (positive) or sink (negative).

Solving Richards’ equation for a dependent variable of pressure (\(p\)) provides features for specifying the values of the hydraulic head or pressure head on the boundaries of a model.

The fluid velocity across the faces of an infinitesimally small surface is:

\[
u = -\frac{k_s}{\mu} k_r \nabla (p + \rho gh)
\]

Dividing \(u\) by the volume liquid fraction, \(\Theta\) characterize the average fluid velocity in the pores (\(u_a = u/\Theta\)). As following, the saturation was defined with the van Genuchten equations:

\[
\theta = \begin{cases} 
\theta_r + s_e (\theta_s - \theta_r) & H_p < 0 \\
\theta S & H_p \geq 0
\end{cases}
\]

\[
s_e = \begin{cases} 
\left( 1 + |aH_p|^{1-m} \right)^{-m} & h_p < 0 \\
1 & h_p \geq 0
\end{cases}
\]

Specific capacity (\(C\)) and relative permeability (\(k_r\)) for using in Eq.1 was defined as following:

\[
c = \begin{cases} 
\frac{am}{1-m} (\theta_s - \theta_r) s_e^{1/m} (1 - s_e^{1/m})^m & H_p < 0 \\
0 & H_p \geq 0
\end{cases}
\]

\[
k_r = \begin{cases} 
 s_e \left( 1 - (1 - s_e^{1/m})^m \right)^2 & h_p < 0 \\
1 & h_p \geq 0
\end{cases}
\]

In Eq. 3 to 6, constants \(a, n, m, \) and 1 specify a particular medium type, and \(HP = p/(\rho g)\) is pressure head, also \(\theta r\) and \(\theta s\), are residual and saturated liquid volume fractions.

3. Solute Transport

The following equations for the concentrations \(c_i\) describe the transport of solutes in variably saturated porous media for the most general case, when the pore space is primarily filled with liquid but also contain pockets or immobile gas:

\[
\frac{\partial}{\partial t} (\theta c_i) + \frac{\partial}{\partial t} (\rho_b c_{pi}) + \frac{\partial}{\partial t} (a_v c_{Gi}) + \nabla (c_i u) = \nabla \cdot \left[ \left( D_{di} + D_{ei} \right) \nabla c_i \right] + R_i + s_i
\]

Here \(c_i\) denotes the concentration of species \(i\) in the liquid (mass per liquid volume), \(Cp\) the amount adsorbed to solid particles (mass per dry unit weight of the solid), and \(cG\) the concentration in the gas phase (mass per volume gas). The equation for bulk density and gas volume fraction are:

\[
P_b = (1 - \theta_s) P_p
\]

\[
a_v = \theta_s - \theta
\]
where \( \rho_p \) is the solid phase density and \( 0_s \) is the pore volume fraction (dimensionless).

On the left-hand side of Eq. 7, the first three terms correspond to the accumulation of species mass within the liquid, solid, and gas phases, while the last term describes the convection due to the directional velocity \( \mathbf{u} \). On the right-hand side, the first term introduces the spreading off mass from to mechanical mixing (dispersion), as well as from diffusion and volatilization to the gas phase. The tensor is denoted \( \mathbf{D}_e \) and the effective diffusion by \( \mathbf{D}_e \). The last two term describe production or consumption of the species; \( \mathbf{R} \), is a reaction rate expression.

In order to solve for the solute concentration of species \( i \), \( C_i \), the solute mass sobbed to solids \( C_{pi} \) and dissolved in the gas-phase \( C_{G,i} \), are assumed to be functions of \( C_i \). Expanding the time-dependent terms:

\[
\frac{\partial}{\partial \tau}(\theta c_i) + \frac{\partial}{\partial \tau}(P_b c_{pi}) + \frac{\partial}{\partial \tau}(a_v C_{G,i}) = \left( \frac{\partial c_i}{\partial \tau} \right) + \left( 1 - K_{Gi} \right) C_i \frac{\partial \theta}{\partial \tau} + (K_{Gi} C_i - P_b C_{pi}) \frac{\partial \theta}{\partial \tau}
\]

where \( k_{pi} = \frac{\partial c_i}{\partial t} \) is the sorption isotherm and \( k_{Gi} = \frac{\partial c_{G,i}}{\partial c_i} \) is the linear volatilization.

\[
(\theta + P_b K_{pi} + a_v K_{Gi}) \frac{\partial c_i}{\partial \tau} + (1 - K_{Gi}) C_i \frac{\partial \theta}{\partial \tau} + (K_{Gi} C_i - P_b C_{pi}) + \nabla(C_i \mathbf{u}) = \nabla \cdot [(D_{Di} + D_{ei}) \nabla c_i] + R_i + S_i
\]

3.1. Sorption

The physics interface predefines three relationships to predict the solid concentrations, \( C_{pi} \), from the concentration in the liquid phase, \( c_i \):

\[
C_p = K_F C^N
\]

\[
C_p = \frac{K_{LS} C}{1 + K_L C}
\]

3.2. Dispersion

In the solute Transport interface dispersion is controlled through the dispersion tensor \( \mathbf{D}_e \). The tensor formulation by Burnett and Friend can be used:

\[
D_{LXX} = a_1 \frac{u^2}{|u|} + a_2 \frac{v^2}{|u|} + a_3 \frac{w^2}{|u|}
\]

\[
D_{LYY} = a_1 \frac{v^2}{|u|} + a_2 \frac{u^2}{|u|} + a_3 \frac{w^2}{|u|}
\]

\[
D_{LXY} = D_{LYX} = (a_1 - a_2) \frac{uw}{|u|}
\]

Here the fluid velocities \( u \), \( v \), and \( w \) correspond to the components of the velocity vector \( \mathbf{u} \) in the \( x \), \( y \), and \( z \) directions, respectively, and \( a_1 \) is the longitudinal dispersivity. If \( z \) is vertical, \( a_2 \) and \( a_3 \), are the dispersivities in the transverse horizontal and transverse vertical directions, respectively.

3.3. Diffusion

In the mass transport in porous media interface, the effective diffusivities are defined as:

\[
D_e = \theta \tau_L D_L + a_v \tau_G D_G
\]

Here \( DL \) and \( DG \) are the single phase diffusion coefficients for the species in the liquid and gas phase respectively, and \( LL \) and \( LG \) are the corresponding tortuosity factors.

\[
\tau_L = \theta^{7/3} \theta_s^{-2}
\]

\[
\tau_G = a_v^{7/3} \theta_s^{-2}
\]

3.4. Chemical Reactions
Chemical reactions of all types influence solute transport in the environment. Examples include biodegradation, radioactive decay, and transformation to tracked products, temperature- and pressure-dependent functions, exothermic reactions, and endothermic reactions. The reactions represent change in solute mass per unit volume porous medium per time. For reactions in a liquid phase, multiply the expression by the liquid volume fraction $\theta$.

$$R_l = \theta r_l$$ (20)

Here $r_l$ is a reaction rate respectively.

With adding microorganism to the underground water, the hydrocarbon compounds were biodegraded into carbon dioxide and methane [14]. Anaerobic microorganisms produce enzymes in the presence of carbon sources which are responsible for attacking the hydrocarbon molecules.

$$4C_nH_m + (4n - m)H_2O \rightarrow \left(\frac{4n-m}{2}\right)CO_2 + \left(\frac{4n-m}{2}\right)CH_4$$ (21)

The general formula of the chemical reaction kinetic that can be described as the rate of Total Petroleum Hydrocarbon (TPH) reduction is:

$$r_i \left[\frac{mg}{lit.day}\right] = \frac{dc_i}{dt} = -k^n_i$$ (22)

Considering the values of reaction orders (n) and reaction rate constants (k), the biodegradation rate is function of pollutant concentration.

Bambang et al. reported reaction rates parameters (k, n) for contaminated soil biodegradation by using of some batteries. As shown in Table 1, Xanthobacter Autotrophicus bacteria could degrade the petroleum oil sludge faster than the others [15].

| Bacteria                  | Reaction order (n) | Reaction constant (k) [day^{-1}] |
|---------------------------|--------------------|----------------------------------|
| Xanthobacter Autotrophicus| 0.8823             | 0.0324                           |
| Pseudomonas pseudoalcaligenes| 1.0949            | 0.00189                          |
| Bacillus Mec_gaterium     | 1.3985             | 0.0204                           |

Suarez and Rifai reported first-order (n=1) biodegradation rates for select petroleum hydrocarbon compounds in groundwater [13]. The reaction constants for biodegradation of different hydrocarbons have been shown in Figure 1.
Figure 1: The reaction rate constants of bioremediation reaction for important pollutants
As shown in Figure 1, reaction constant for each pollutant varies with temperature, microorganism type and other parameters. Also Buscheck and Alcantar introduced porous media structure effect on reaction rate constant [16].

4. Experimentation
In this work, an experimental setup prepared for producing valuable data. As shown in Figure 2, a sand pack surrounded with two pools (injection and removal wells) is used for studying pollutant distribution in porous media. Sand pack jointed into pools with couple of sintered filters. The Autotrophicus bacterium was used for biodegradation of oil pollutant. During of experimentation concentration of bacterium is measured and adjusted in specific times. In the injection well, microorganism medium which is needed for their cultivation was controlled by measuring online concentrations of major components in the well every 8 hours. The cultivation medium of Also for reproducing of pollutant zone, pollutant droplet is added for considered zone manually. The used pollutant is synthetically petroleum oil-water solution. Rain fallen (surface water) is simulated in experimental setup with parallel distributors and water supply system. In the removal well contaminant concentration is measured with preparing chemical analysis samples. Physical properties of porous media were shown in Table 2.

Figure 2. The schematic of experimental setup for bioremediation process
Table 2. The used physical properties in the numerical modeling.

| Parameter      | unit | value      |
|----------------|------|------------|
| Conductivity   | m/s  | 2.94x10^- |
| Voidage        | -    | 0.35       |
| Bulk density   | Kg/m³| 1400       |
| Height         | m    | 0.2        |
| Width          | m    | 1          |

5. Results

Numerical modeling of the pollutant dispersion in a porous media is carried out using indoor CFD code based on finite difference method. As shown in Figure 3, the calculation domain is a rectangle porous media that proposed for computation has width and height of L=1.0 and H=0.2m, respectively. The domain was divided into uniform 20x100 grids. Also, the simulation was continued for 3*10^5 second with time steps equal to 100 second. Here the grid independence is tested by varying the density of computational domain. The grid refinement was continued until the solution parameters such as time averaged pressure drop showed no variations. As discussed previously, physical properties were introduced to the numerical modeling proportional to the experimental work (Table 2). Boundary conditions (B.C.s) for solving of partial differential equations of numerical model (Eq. 1, 11) were listed in Table 3, too.

![Figure 3](image-url)

Figure 3. Numerical domain with considered boundary conditions

Table 3. the proposed boundary conditions in the numerical modeling

| Surface | B.C.s for hydraulic head | B.C.s for ith pollutant and microorganism transport |
|---------|---------------------------|---------------------------------------------------|
| 1       | h=0.1m                    | Ci=0, Cmic=0                                      |
| 2       | dh/dz=0, Isolated         | de/dz, Dc                                        |
| 3.5     | u=1*10^-6 m/s *           | C=If, Cmic=0                                     |
| 4       | u=1*10^-6 m/s *           |                                                   |
| 6       | h=0.05m                   | Dc/dx, Dc                                        |

5.1. Water velocity

As shown in Figure 4, superficial velocity of water in the porous media increases with time. At first, water saturation in the aquifer starts to increase and velocity of water reaches to the steady flow condition. At t=1.65x10^5s (=:02day) an epoch point occurs in velocity trend. Due to a synthetic pressure (or head) gradient within the aquifer that is produced by pump, the water velocity increases
with approach of the surface water into aquifer. From Figure 4 it can be find that experimental and model results are in good agreement. Before the epoch point, underestimate of modeling results is because of higher capillary anticipation in the model that prevents entering of water and pushing of trapped air through the porous media or using the lower conductivity value in the modeling. Likewise, after the epoch point upper estimate of model could be due to ignoring of surface evaporation at top of the porous media.

![Figure 4](image1.png)

**Figure 4.** The result of numerical and experimental superficial water velocity along the porous media.

The velocity counter of water flow at $t=3\times10^5\,\text{s}$ was presented in Figure 5. In addition, the surface water velocity was shown with downer come vectors and aquifer water velocity with declined vectors. It is obvious that the water velocity increases along the aquifer due to addition of the surface waters and decreasing of water table that achieved with hydraulic head gradient.

![Figure 5](image2.png)

**Figure 5.** Numerical result of water velocity and saturation distribution.

5.2. *Contaminant dispersion*

Component molar flux $(c,u)$ is an important parameter in mass transfer and finding mass dispersion within a medium. The mass flux multiplying by the crossing area of pollutant gives flow rate of pollutant dispersion in the domain. In Figure 6, contour of pollutant molar flux distribution was shown. Through the unsaturated zone of the porous media, the pollutant introduces to movement with surface water flow. The pollutant penetrates, rises down and reaches to water table (boundary of saturated and unsaturated zones). Fortunately, through the aquifer, the water flow is laminar flow and lower convectional mass transfer occurs in deep direction of aquifer. It is obvious that the larger amount of pollutants is gathered in water table.
The water table is the contact line of air and water. Then, this is a potential point to application of microorganisms for biodegradation of pollutants within the aquifers, because air could be supplied easier than water saturated zone.

Space/stay time is time required to process one reaction volume of feed that is measured at specified conditions. Here, the reaction volume is aquifer and feed is entered microorganism at injection well. It is obvious that reaction progress increases with increasing of space time and biodegradation yield increases. On the other hand, space time has an inverse relation with entering flow rate of injection well ($\tau = (V/\theta)$). This means that higher space time that could be reached with lower injection flow rates that causes the pollutant dispersion in unwanted direction, because pollutant have enough time to diffusion in all directions, and it is not desired. In Figure 7, pollutant flux (measured in removal well) is plotted versus time at various positive heads of injection that produces various entering flow rate in injection well. Also, for showing effect of microorganism, results of a case study without using of microorganism have been shown in Figure 7. As shown, with increasing injection positive head (gives higher flow rate of entering flow) decreases space time and lower biodegradation takes place. In Figure 7, for a specific entering flow rate (head=5m), biodegradation reaction reduced pollutant dispersion flux which presents microorganism performance in the aquifer. Diversion from experimental results were increased with increasing entering positive head, it can be due to non-Darcy flows. For this cases, the head equation (Eq.1) should be modified and with reduction of errors in prediction of velocity profiles better agreement between model and experimental results could be reached.
6. Conclusion
In this work, experimental and numerical studies have been done on clarifying of pollutant dispersion in the underground water sources; also the remediation process was introduced for controlling of contaminant growth. The modeling results validated for water velocity within porous media that was proposed for experimentation. In addition, it is found that the pollutant dispersion is concentrated on water table, and accumulation of pollutant is lower in other points of saturated zone. Likewise, space time goes down with flow rate of entering flow and as a result lower biodegradation takes place. Moreover, biodegradation reaction cause to reduction of pollutant dispersion flux that shows better microorganism performance in the aquifer.

7. References
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