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Abstract

A simplified numerical algorithm was developed to solve the nonlinear Monod-kinetics for an organic contaminant, oxygen, nitrate, and microbial population. The numerical algorithm is presented in the batch-reactor mode and the accuracy and efficiency of the algorithm were tested with an iterative solution using the Runge–Kutta method. The results showed a good match between the two solutions with a high computational efficiency. The applicability of the algorithm was further tested using a field-scale example of natural attenuation where the algorithm was coupled with the advective-dispersive transport equations. The results showed remarkable computational efficiency of the algorithm in solving the nonlinear coupled transport equations to the extent of ready-applications in field-scale remediation designs.

1 Introduction

Bioremediation is a commonly used cleanup technology in organic-contaminated subsurface during the past decade. However, quantitative analysis of biodegradation of organic contaminants is complex due to nonlinear degradation kinetics (Borden and Bedient, 1986; Kinzelbach et al. 1991). Due to this reason, most field-scale designs have used simplified 1st-order kinetics, but such a representation cannot demonstrate the various limiting factors associated with the biodegradation process. The main advantage of using nonlinear Monod-kinetics is that analysis can consider the limiting factors such
as nutrients or electron-acceptors under varying geo-chemical and biological conditions. The major drawback is that the system of equations is complex and computationally intensive. The goal of this work is to present a simplified, efficient and an accurate numerical algorithm that can represent Monod-kinetics based biodegradation of organics using oxygen and nitrate as electron-acceptors, and microbes.

2 Theoretical Development

The assumptions used in the model development are (1) no nutrient limitations; (2) sequential electron-acceptor use from oxygen to nitrate with a threshold oxygen concentration of $O_T$; (3) complete mixing of all species and no limitations due to diffusion or bio-availability; (4) metabolism is controlled by lack of substrate or electron-acceptors; and (5) no lag time for switching from oxygen to nitrate.

Subjected to the above assumptions, biological decay of an organic contaminant in the presence of oxygen, nitrate, and microbes can be represented using Monod-kinetics as

$$\frac{dC}{dt} = -\frac{V_{AER}}{Y_{AER}} \cdot \frac{C}{K_{CAER} + C} \cdot \frac{O}{K_O + O} \cdot X \cdot (1 - S(O)) - \frac{V_{DEN}}{Y_{DEN}} \cdot \frac{C}{K_{CDEN} + C} \cdot \frac{N}{K_N + N} \cdot X \cdot S(O)$$  \hspace{1cm} (1)

$$\frac{dO}{dt} = -\frac{V_{AER}}{Y_{AER}} \cdot \frac{C}{K_{CAER} + C} \cdot \frac{O}{K_O + O} \cdot X \cdot (1 - S(O)) \cdot F_O$$  \hspace{1cm} (2)

$$\frac{dN}{dt} = -\frac{V_{DEN}}{Y_{DEN}} \cdot \frac{C}{K_{CDEN} + C} \cdot \frac{N}{K_N + N} \cdot X \cdot S(O) \cdot F_N$$  \hspace{1cm} (3)

$$\frac{dX}{dt} = \frac{V_{AER}}{K_{CAER} + C} \cdot \frac{O}{K_O + O} \cdot X \cdot (1 - S(O)) + \frac{V_{DEN}}{K_{CDEN} + C} \cdot \frac{N}{K_N + N} \cdot X \cdot S(O) - \frac{V_{DEC}}{X} \cdot X$$  \hspace{1cm} (4)

where $t$ is the time [T]; $C$ is the dissolved contaminant concentration [ML$^{-3}$]; $O$ is the dissolved oxygen concentration [ML$^{-3}$]; $N$ is the dissolved nitrate concentration [ML$^{-3}$]; $X$ is the dissolved microbial concentration [ML$^{-3}$]; $S(O)$ is the oxygen dependent switching function; $O_T$ is the threshold oxygen concentration for switching from oxygen to nitrate [ML$^{-3}$]; $V_{AER}$ is the maximum microbial growth rate for aerobic metabolism [T$^{-1}$]; $V_{DEN}$ is the maximum microbial growth rate for denitrification [T$^{-1}$]; $V_{DEC}$ is the...
microbial decay coefficient \([T^{-1}]\); \(Y_{AER}\) is the yield coefficient for aerobic metabolism \((MM^{-1})\); \(Y_{DEN}\) is the yield coefficient for denitrification \((MM^{-1})\); \(K_{CAER}\) is the half saturation constant of the contaminant for aerobic metabolism \([ML^{-3}]\); \(K_{CDEN}\) is the half saturation constant of the contaminant for denitrification \([ML^{-3}]\); \(K_{O}\) is the half saturation constant of oxygen for aerobic metabolism \([ML^{-3}]\); \(K_{N}\) is the half saturation constant of nitrate for denitrification \([ML^{-3}]\); \(F_{Q}\) is the mass ratio of oxygen consumed per unit mass of contaminant consumed (without allowance for cell synthesis); and \(F_{N}\) is the mass ratio of nitrate consumed per unit mass of contaminant consumed (without allowance for cell synthesis). The switching function \(S(O)\) is defined as \(S(O)=0\) for \(O>O_{T}\) or \(S(O)=1\) for \(O\leq O_{T}\). Also where linear equilibrium adsorption of contaminant, nitrate, or microbes is present, the appropriate values of \(V_{AER}\), \(V_{DEN}\), and \(V_{DEC}\) can be defined as apparent values by dividing the corresponding retardation coefficient.

### 2.1 Simplified Algorithm for Solution of Reaction Terms

The proposed algorithm is applied at each time step of the numerical solution scheme. In order to evaluate the consumption pattern over a given time step, several initial calculations are performed. These computations are used to determine suitable linear interpolations to nonlinear Monod-kinetics. The algorithm is discussed using oxygen as the electron acceptor. Once the use of oxygen is accomplished in a given time step and if time remains, then use of nitrate will follow. The calculations with nitrate will be the same as described below except that oxygen has to be replaced by nitrate with appropriate values of all bio-kinetic parameters. The proposed simplified algorithm branches into two major sections based on the contaminant and electron acceptor concentrations, and the half-saturation constant of the contaminant. The branching is due to the fact that biodegradation rates can vary from slow to fast depending on the existing conditions. The two conditions separating the different biodegradation rates were obtained using a series of simulations using the exact solution on a variety of conditions. The details related to one of the two limiting conditions is described in the next section and the units of concentration are in mg/L.

#### Case A: \(O<6\) or \(C<K_{CAER}+1\)

It was observed that for relatively low oxygen and/or contaminant concentrations satisfying \(O<6\) or \(C<K_{CAER}+1\), the times required to consume \(O\) and \((O-O_{T})\) can be approximated reasonably accurately. First, the amount of contaminant concentration, \(C_{3}\), that can be stoichiometrically degraded by oxygen over the given time step, is calculated as \(C_{3}=O/F_{O}\). Second, the time required to consume \(O\) or to degrade \(C_{3}\), defined as \(T_{3}\), can be approximated through the rearrangement of Equation (1) as follows:
\[
T_3 = \frac{C_3}{V_{AER} \cdot C \cdot O \cdot X} \cdot \frac{1}{Y_{AER} \cdot (K_{CAER} + C) \cdot (K_O + O)}
\]  

Similarly, if the amount of contaminant that can be degraded by (O-O_T) is defined as \(C_2\) and the time required to consume (O-O_T) or degrade \(C_2\) is defined as \(T_2\) where \(C_2 = (O-O_T)/O_o\) and

\[
T_2 = \frac{C_2}{V_{AER} \cdot C \cdot (O - O_T) \cdot X} \cdot \frac{1}{Y_{AER} \cdot (K_{CAER} + C) \cdot (K_O + (O - O_T))}
\]  

It was found from detailed numerical simulations that \(T_2\) may overestimate the actual time required to decay \(C_2\) and therefore, \(T_2\) needs to be adjusted. The detailed numerical simulations indicated that this overestimation can be corrected by using 67% of the computed \(T_2\). If \(C < K_{CAER} + 1\) and \(C_2 > C\), then \(T_2\) needs to be calculated alternatively as

\[
T_2 = \frac{C}{V_{AER} \cdot C \cdot (O - O_T) \cdot X} \cdot \frac{1}{Y_{AER} \cdot (K_{CAER} + C) \cdot (K_O + (O - O_T))}
\]

In this work, it was assumed that after the switch from oxygen to nitrate, the use of oxygen ceases and therefore, \(O\) is consumed only up to the value of \(O_T\). Hence, \(C_3\) and \(T_3\) are not used unless simultaneous use of oxygen and nitrate is required in the vicinity of \(O_T\). However, if \(T_2 > T_3\), then \(T_2\) is replaced by \(T_3\).

New microbial concentration corresponding to \(T_2\) and \(C_2\) which is denoted as \(X_2\) can be linearly approximated by the following equation

\[
X_2 = X + Y_{AER} \cdot C_2 - V_{DEC} \cdot X \cdot T_2
\]  

which was obtained by manipulating Equations (1) and (4) and substituting \(dC = C_2\), \(dt = T_2\), and \(dX = X_2 - X\). Now that initial values of \(C\), \(O\), and \(X\), and the values of \(C\), \(O\), and \(X\) after time \(T_2\) are known, the slopes between concentration and time can be calculated. Referring to Figure 1, the slope of the line through \((0,C)\) and \((T_2,C_2)\) is \(MC_2 = -C_2/T_2\). Similarly, for oxygen and microbes, the slopes are \(MO_2 = MC_2\), \(F_O\) and \(MX_2 = (X_2 - X)/T_2\), respectively. A qualitative plot of concentration vs. time for Case A where \(O < 6\) or \(C < K_{CAER} + 1\) is shown in Figure 1. The plot shows the two points corresponding to \((T_2, C_2)\) and \((T_3, C_3)\) for both exact solution obtained from
the iterative solution and the profile approximated by the simplified algorithm. The plot also shows the minimum oxygen concentration needed to support the microbial growth, OM, O_T, and the oxygen concentrations remaining after times T_2 and T_3. In the present study, we assumed OM=0, but in applications, there is no restriction to consider values of OM>0. A similar procedure is followed for the Case B where O_geq 6 and C_geq K_{CAER}+1. However due to space limitation, this case will not be discussed and the reader is encouraged to contact the authors for more information.

Figure 1. Qualitative plot of concentration versus time to describe the simplified numerical algorithm.

3 Examples Simulations

3.1 Batch-Reactor Simulation
This example was selected to demonstrate the applicability of the proposed simplified algorithm to bio-kinetic parameters satisfying Case A. The representative contaminant used here was toluene as it is degraded by both oxygen and nitrate. The initial concentrations of toluene, oxygen, nitrate, and microbes used were 20, 2, 20, and 0.5 mg/L, respectively. The values of bio-kinetic parameters were K_{CAER}=K_{CDEN}=8 mg/L, Q_T=0.2 mg/L, K_O=K_N=0.2 mg/L, Y_{AER}=0.09, Y_{DEN}=0.1, V_{AER}=V_{DEN}=2.3\times10^{-4} \text{ sec}^{-1}, \text{ and } V_{DEC}=2.3\times10^{-6} \text{ sec}^{-1}. The initial microbial concentration was assumed 0.5 mg/L. The simulation time was 2 days with a time step of 0.02 days. The computational time for the simplified algorithm was approximately 1 seconds and whereas the corresponding value for the exact solution was 12 seconds. Figure 2 shows the distribution of toluene, oxygen, nitrate, and microbial population with time. The results show a good agreement for oxygen and an acceptable agreement for nitrate, contaminant and microbes. In all four species, the simplified algorithm showed earlier arrival or depletion of a given species compared to
the concentrations produced by the exact solution. The solution using the simplified algorithm managed to capture the key features of the biodegradation process. For example, as the oxygen depleted, the nitrate consumption commenced and during these reactions, the growth of the microorganisms occurred. After both electron acceptors were exhausted, the microorganisms underwent natural decay and the contaminant concentration remained constant.

![Figure 2. Concentration versus time results for the batch-reactor example.](image)

3.2 Natural Attenuation of Toluene in a Two-Dimensional Aquifer

The simplified numerical algorithm was incorporated in to a modified version of USGS flow and transport model, SUTRA to simulate advective-dispersive-reaction transport with multiple species. The operator-splitting technique (Morshed and Kaluarachchi, 1995) was used to simulate the coupling between the transport and reaction parts. The problem consists of a 850 feet long, 400 feet wide, and a 25 feet deep aquifer. The plume area is 350 feet long and 200 feet wide and starts 150 feet from the upstream. The domain was discretized using 25x25 feet² elements. Porosity, hydraulic conductivity, longitudinal dispersivity, and transverse dispersivities were 0.3, 11.5 feet/day, 25, and 2.5 feet, respectively. The species were assumed non-retarded. The bio-kinetic parameters were $F_o=3.13$, $F_N=4.72$, $K_{CAER}=K_{CDEN}=8 \text{ mg/L}$, $K_o=K_N=0.2 \text{ mg/L}$, $Y_{AER}=0.09 \text{ mg/L}$, $Y_{DEN}=0.1 \text{ mg/L}$, $V_{AER}=V_{DEN}=2.31\times10^{-5} \text{ sec}^{-1}$, and $V_{DEC}=2.31\times10^{-6} \text{ sec}^{-1}$. The initial toluene within the contaminated zone, oxygen, nitrate, and microbial concentrations were 50, 8, and 20, and 0.5 mg/L, respectively. Figures 3 and 4 show the concentration distributions of all four species after one year along the longitudinal centerline of the domain where there is a good match between the simplified and the exact solutions. Finally, a series of simulations using the simplified model was conducted by
changing the time step from the base case value of 3 days to evaluate the computational efficiency of the proposed scheme. The results of these simulations are shown in Table 1. Comparison of simulation times shows a substantial CPU time saving with the simplified solution over the exact solution.

Figure 3. Concentrations of different species after one year for the natural attenuation example where the exact solution is in solid and the simplified solution is in dash lines; (a) Toluene (C) and Oxygen (O), and (b) Nitrate (N) and Microbes (X).
Table 1. CPU times used in the natural attenuation example using a Pentium 75 PC.

<table>
<thead>
<tr>
<th>Δt (days)</th>
<th>CPU Time (minutes)</th>
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<tbody>
<tr>
<td></td>
<td>Exact</td>
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<tr>
<td>0.1</td>
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<tr>
<td>1</td>
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4 Conclusions

A simplified numerical algorithm was proposed to solve the nonlinear and coupled reaction equations describing biodegradation of organic contaminants using Monod-kinetics. The solution scheme was used to solve degradation of toluene using oxygen and nitrate in a batch-reactor example and a field-scale natural attenuation problem. The results showed good accuracy between the simplified algorithm and the iterative solution and a three to four fold decrease in computational effort. Due to the substantial reduction of computational effort, the proposed algorithm is suited for detailed field-scale simulations for bioremediation designs.

5 References

