Modeling of Reductive Biodegradation of TCE to ETH

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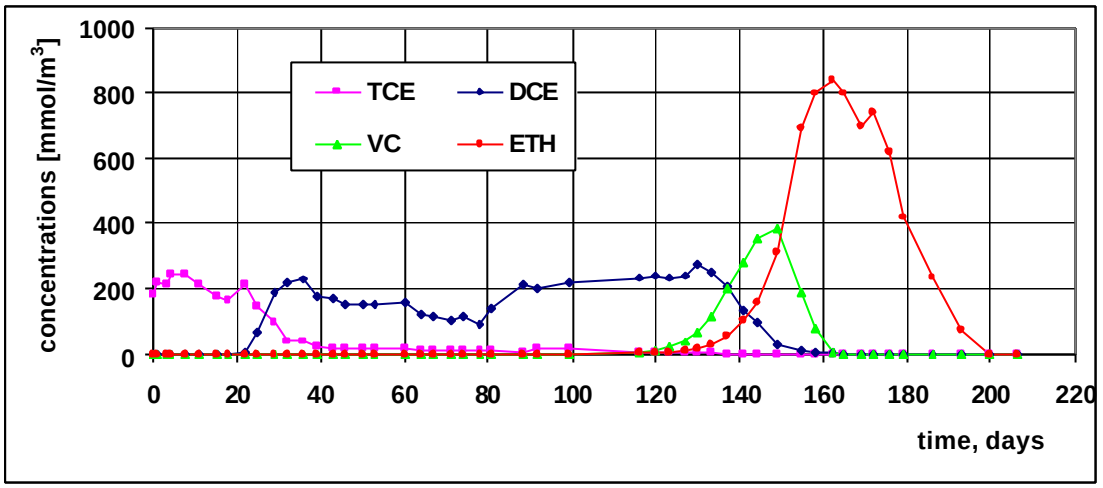
Abstract
A reductive bioremediation process of chlorinated solvent (TCE) was modeled using kinetic approach. Degradation of TCE to ETH was considered as a consecutive set of biochemical transformations. Experimental data were used for process analysis and assessing order of each process step. It was assumed, that biochemical reactions control overall quickness of the process. According to results of experiments model was divided into two parts TCE ? DCE and DCE ? VC ? ETH conversion. Small bioreactor gas leakage, detected during experiment, was incorporated in model equations. Analytical solutions were determined and calculations were compared to experimental data. Model was enhanced to include biological nature of analyzed processes: a logistic equation was used to describe kinetic parameter dependency on microorganisms' population. Calculations performed with enhanced model equations were compared to experimental data with satisfactory results.

Introduction
Using and disposal of volatile organic compounds (VOC) often result in soil and ground water environmental problems. Chlorinated solvents, such as tetrachloroethene (PCE), trichloroethene (TCE), trichloroethane (TCA) and carbon tetrachloride (CT) are considered to be one of the most environmentally dangerous VOCs. Among few technologies which are capable of removing those compounds from soil and groundwater, bioremediation seem to be relatively cheap and environmentally friendly. Transformation of chlorinated solvent during biodegradation process can follow either reductive dehalogenation (halorespiration) or oxidation reactions (aerobic and anaerobic oxidation).
A typical reductive dechlorination process of TCE can be treated as a set of three steps, consequent reactions. The TCE is first converted to *cis* and *trans* dichloroethene (DCE). DCE is then converted to vinyl chloride (VC) and VC is changed into ethylene (ETH) which ends the degradation path.
Modeling biodegradation of TCE to ETH involves analysis of possible biochemical reactions in a particular bioremediation system, experimental data analysis, making reasonable simplifying assumption and formulating set of equations describing considered system. Once the equations are formulated and parameters are assessed, calculations are made and model is verified with experimental data.

Experimental Background
A small, pocked bad, continuous gas recirculation bioreactor was developed in Institute for Ecology of Industrial Areas (Poland) with cooperation with Westinghouse Savannah River Company (USA) to clean up a limited (up to 3 cubic meters) amounts of TCE contaminated soil. The system was designed to take advantage of anaerobic biodegradation of TCE and is equipped with process monitoring and controlling system. Periodically, samples of soil gases were taken for laboratory analysis. As the process was carried out in anaerobic conditions, taking soil samples was impossible. Figure 1 presents measured average TCE, DCE, VC and ETH concentration changes in soil gases. The results obtained during biodegradation experiment were uses as a basis for formulation of mathematical process description. It was assumed that equilibrium in TCE, DCE, VC and ETH concentrations among gas, liquid and solid-adsorbed phases are maintained through process duration. On that basis, calculating of total amount of each compound can be done by using appropriate Henry's law and adsorption constants, providing that volume of each phase is known.

Figure 1. TCE, DCE, VC and ETH mean concentration in soil gas.



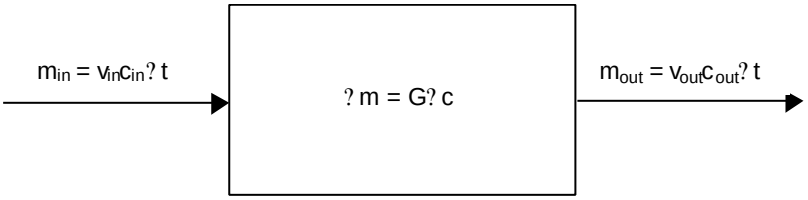
Model formulation

Results of experiment prove the consecutive character of assumed reactions set. Three different periods can be identified in the bioreactor operation:

- Sharp decrease of TCE concentration (after short period of stable concentration) accompanied with distinct increase in DEC concentration, concentrations of VC and ETH were negligible;
- Negligible concentrations of TCE, close to zero concentrations of VC and ETH but slow increase may be observed at the end of the period, DCE concentration tend to decline when VC end ETH begun to rise;
- TCE concentration negligible, decrease of DCE concentration to zero, VC concentration gained a maximum and then dropped to very small values. The concentration changes of ETH were similar but the maximum was higher and shifted in time.

Because TCE to DCE transformation was separated from further transformation of DCE to ETH through VC, the model was divided into two parts: (i) description of TCE to DCE reaction and (ii) description of consequent DCE to VC and then to ETH reactions. As ETH was a final product of the reductive biodegradation of TCE and no signs of ETH degradation products were found, it was assumed that observed decrease in ETH concentration was caused by gas leakage from the bioreactor vessel. Gases (mostly CO2 and O2) production during reductive degradation of sludge was considered as a driving force for pressure increase inside the vessel, and, in consequence, gas leakage. It was assumed that gas escape took place during whole bioremediation process. Changes in gas phase concentration of chlorinated aliphatic compounds are schematically illustrated in the figure 2:

Figure 2. Changes in gas phase concentration of chlorinated aliphatic compounds schema



where:

m_{in}, c_{in} – mass and concentration of chlorinated aliphatic compounds flowing into the reactor over time $?t$

v_{in} – flow rate of gases into the reactor (in this case – the rate of gases generation in sludge degradation)

m_{out}, c_{out} – mass and concentration of chlorinated aliphatic compounds flowing out of the reactor over time $?t$

v_{out} – flow rate of gases leaking from the reactor

$?m$, $?c$ – increase in chlorinated aliphatic compounds mass content and concentration in the reactor gas phase over time $?t$

G – gas phase volume in the reactor.

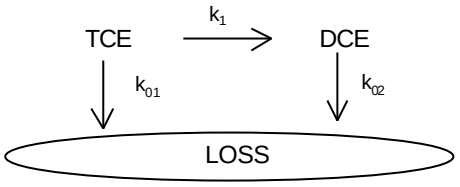
Mass balance equation for gas volume in the bioreactor may be written in the form:

$$? m ? G? c ? ? _{in} c_{in} ? t ? ? _{out} c_{out} ? t$$

As the flowing gases does not contain any chlorinated compounds, c_{in} = 0. Rearranging above equation and substituting cin = 0:

$$\frac{? c}{? t} ? ? \frac{? _{out}}{G} c_{out} ? \; ? _{t ? 0} ? \; ? \frac{dc}{dt} ? \frac{? _{out}}{G} c ? k_{0c} c$$

which shows, that loose of chlorinated aliphatic compounds caused by gas leakage can be described by first order kinetic equation. The formula is also true in case of ETH.
The process of TCE to DCE reductive biodegradation, including looses(firs part of whole process), can be depicted as follows:



Assuming that TCE to DCE degradation process can be described by zero order kinetics, the following set of ordinary differential equations can be formulated:
The initial values for TCE is equal its beginning content in the vessel and for DCE and LOSS is zero.

$$\frac{d n_{TCE}}{d t} ? ? (k_1 ? k_{01} n_{TCE})$$

$$\frac{d n_{DCE}}{d t} ? k_1 ? k_{02} n_{DCE}$$

$$\frac{d n_{LOSS}}{d t} ? k_{01} n_{TCE} ? k_{02} n_{DCE}$$

Analytical solutions of presented above equation can be written as follows:

$$n_{TCE} ? \left(n_{TCE_0} ? \frac{k_1}{k_{01}} \right) e^{? k_{01} t} ? \frac{k_1}{k_{01}}; \quad 0 ? t ? \frac{1}{k_{01}} \ln \frac{n_{TCE_0} ? \frac{k_1}{k_{01}}}{\frac{k_1}{k_{01}}} ? t_k \qquad n_{TCE} ? 0; \quad t ? t_k$$

$$n_{DCE} ? \left(n_{DCE_0} ? \frac{k_1}{k_{02}} \right) e^{? k_{02} t} ? \frac{k_1}{k_{02}}; \; 0 ? t ? t_k \qquad n_{DCE} ? n_{DCE} t_k ? e^{? k_{02} ? t ? t_k ?}; \quad t ? t_k$$

$$n_{LOSS} ? n_{TCE_0} ? ? n_{TCE} ? n_{DCE} ?$$

Comparison between calculated and measured TCE and DCE contents over time are presented in the figure 3
The second part of the TCE reductive biodegradation (dechlorination of DCE followed by dechlorination of VC) is presented on schematic diagram below:

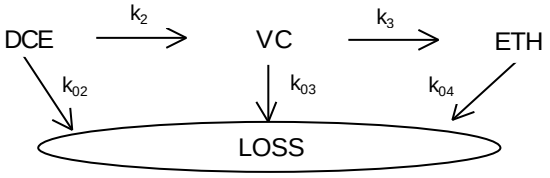
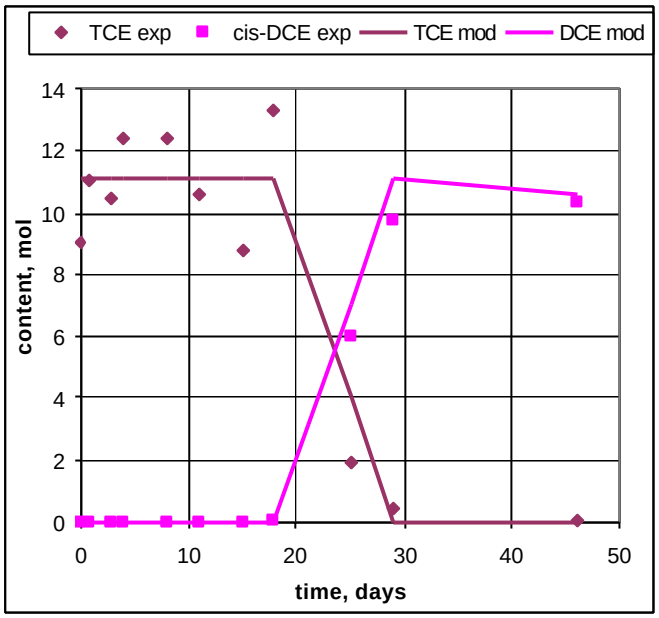


Figure 3. Changes in TCE and DCE contents in the bioreactor over time.



Assuming first order reaction model for DCE as well as VC degradation, the following equations can be obtained:

$$\frac{dn_{ETH}}{dt} = k_3 n_{VC} - k_{04} n_{ETH} \qquad \frac{dn_{LOSS}}{dt} = k_{02} n_{DCE} + k_{03} n_{VC} + k_{04} n_{ETH}$$

$$\frac{dn_{DCE}}{dt} = -(k_2 + k_{02}) n_{DCE} \qquad \frac{dn_{VC}}{dt} = k_2 n_{DCE} - (k_3 + k_{03}) n_{VC}$$

Their analytical solutions can be written as follows:

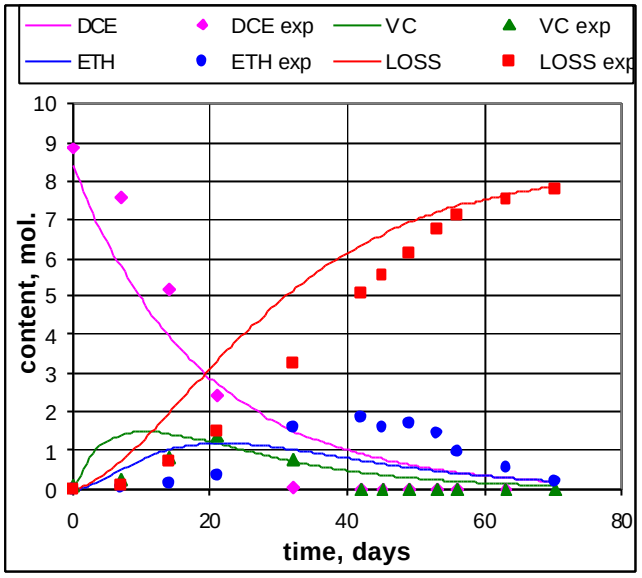
$$n_{DCE} = n_{DCE_0} e^{-(k_2 + k_{02})t} \qquad n_{LOSS} = n_{DCE\,0} - (n_{DCE} + n_{VC} + n_{ETH})$$

$$n_{ETH} = k_2 k_3 n_{DCE\,0} \left[\frac{e^{-(k_2 + k_{02})t}}{(k_{04} - (k_2 + k_{02}))((k_3 + k_{03}) - (k_2 + k_{02}))} + \frac{e^{-(k_3 + k_{03})t}}{(k_{04} - (k_3 + k_{03}))((k_2 + k_{02}) - (k_3 + k_{03}))} + \frac{e^{-k_{04} t}}{((k_2 + k_{02}) - k_{04})((k_3 + k_{03}) - k_{04})} \right]$$

$$n_{VC} = k_2 n_{DCE_0} \left[\frac{e^{-(k_2 + k_{02})t}}{(k_3 + k_{03}) - (k_2 + k_{02})} - \frac{e^{-(k_3 + k_{03})t}}{(k_2 + k_{02}) - (k_3 + k_{03})} \right]$$

Comparison between calculated and measured values is presented in the figure below.

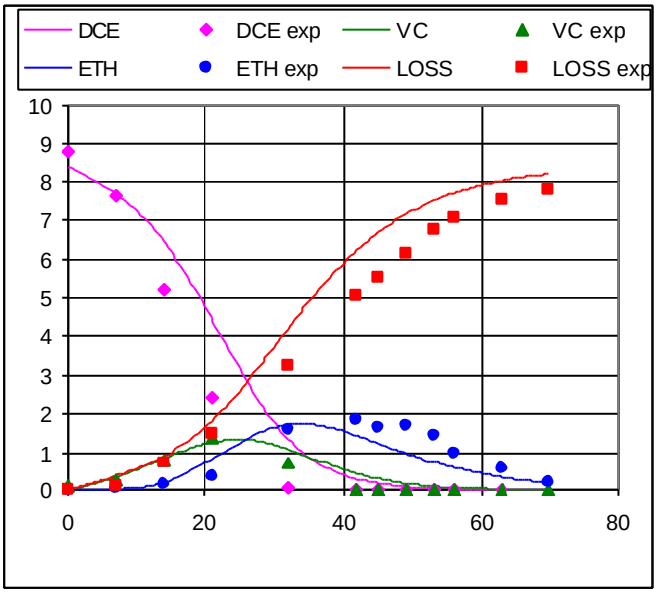
Figure 4. Changes in DCE, VC and ETH contents in the bioreactor over time.



Model enhancement

Assuming that the rate constants are proportional to number of microorganisms active in a given reaction a biological nature of processes may be incorporated. It was additionally assumed that changes in population of microorganisms over the time follows the logistic equation. Applying appropriate modifications to model equations resulted in better model fit to experimental data (fig 5)

Figure 5. Changes in DCE, VC and ETH contents over time – logistic apporoach



Conclusions

Reductive bioremediation of TCE can be modeled as a set of consecutive reactions. Though first order kinetics does not fit well to experimental data, model can be further enhanced. Making kinetic constant proportional to logistic equation results in significant improvement of model fit to experimental data.

Acknowledgements

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