Numerical modelling of the simultaneous degradation of TCE and cis-DCE by zero-valent iron

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Abstract The degradation of TCE, cis-DCE and mixtures of both was investigated in laboratory columns packed with zero-valent iron. Analyses show that TCE degradation is only marginally influenced by the addition of cis-DCE whereas the rate constant for cis-DCE degradation is reduced by a factor of about two upon addition of TCE. A new modelling approach was developed to describe the assumed processes of competitive adsorption, desorption and dechlorination. Parameters determined by Arnold & Roberts (2000) were transferred to the model to extrapolate concentrations of species, which were not measured in our experiments. By fitting these parameters to different experimental set ups, one set of parameters was found that describes the degradation of the single substances TCE and cis-DCE, as well as any mixtures of them.

Key words chlorinated hydrocarbons; competitive adsorption; dechlorination; iron; laboratory study; model parameters; reaction kinetics

INTRODUCTION

The degradation behaviour of chlorinated hydrocarbons in iron permeable reactive barriers (PRBs) has been the subject of several investigations (Gavaskar et al., 1998). Degradation of chlorinated hydrocarbons on iron is a complex surface chemistry problem (Cipollone et al., 1995; Sivavec & Horney, 1995). Dissolved TCE is transported with the natural gradient into a reactive barrier system. For a chemical reaction with iron, TCE must adsorb onto reactive sites of the iron surface. This adsorption/desorption process to a limited surface area is assumed to follow Langmuir kinetics (Fogler, 1992; Zepp & Wolfe, 1987). The adsorbed TCE is dechlorinated by a first-order degradation reaction with respect to the adsorbed TCE concentration. The reaction products chloroacetylene, trans-, cis- and 1,1-DCE produced by this reaction (Fig. 1) are already sorbed onto the reactive iron surface but they can desorb from, or adsorb onto, the iron surface with their own specific kinetic parameters. Adsorbed reaction products can be further degraded to VC, acetylene, ethylene and finally ethane.

Thus, even the degradation of the original substance TCE is not a “single-component” problem. Competing reactions occur during the degradation, since TCE and its degradation products adsorb onto the same reactive iron surface on which they are dechlorinated. The purpose of our study is to investigate the effect of a mixed contaminant load on the degradation behaviour of the single components using a mixture of TCE and cis-DCE. This combination is environmentally important since
TCE as well as \textit{cis}-DCE are often found together, e.g. in aged plumes. A complex modelling approach supported the column studies in the laboratory.

**EXPERIMENTAL SET UP AND MEASUREMENTS**

The set up of the column experiments performed is described in detail in Wüst \textit{et al.} (1999). The column (HDPE, 100 cm length, 10 cm i.d.) was packed with a 5 cm thick sand filter to equilibrate flow and 92 cm granular commercial iron (Hartgusstrahmittle GH-R, Würth, round, diameter 1–1.16 mm). Nine sampling needles with Luer Lok fittings, permanently installed along the column, served for sampling. The effective porosity was determined to be 30%. A flow rate of 1 ml min$^{-1}$ was chosen, resulting in a residence time of about 35 h and a pore velocity of about 61 cm day$^{-1}$.

Initial concentrations of TCE and \textit{cis}-DCE in the injection water for the four experimental stages are shown in Table 1. During each stage approximately 30 pore volumes were exchanged resulting in a quasi-stationary concentration profile. Since the concentrations do not change significantly over time, they are in equilibrium with concentrations adsorbed to non-reactive surfaces. Due to this set up adsorption to, or desorption from, non-reactive sites can be neglected.

First the degradation rates were investigated by performing a regression analysis of the measured concentrations assuming a first order degradation law. Comparison of degradation rates (Table 1) shows that \textit{cis}-DCE is degraded more rapidly than TCE, which is in disagreement with the common assumption of accelerating degradation rate with increasing chlorination. Analyses show that TCE degradation is only marginally influenced by the addition of \textit{cis}-DCE whereas the rate constant for \textit{cis}-DCE degradation is reduced by a factor of about two upon addition of TCE.
Table 1  Average initial TCE and cis-DCE concentrations for the respective stages of the column experiment and first-order degradation rates obtained from regression analysis normalized to a BET-surface/solution ratio of 1.51 m$^2$ ml$^{-1}$.

<table>
<thead>
<tr>
<th>Stage</th>
<th>cis-DCE only</th>
<th>TCE only</th>
<th>TCE and cis-DCE 10:1</th>
<th>TCE and cis-DCE 1:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCE (μmol l$^{-1}$)</td>
<td>-</td>
<td>340</td>
<td>308</td>
<td>281</td>
</tr>
<tr>
<td>cis-DCE (μmol l$^{-1}$)</td>
<td>372</td>
<td>-</td>
<td>29</td>
<td>256</td>
</tr>
<tr>
<td>1st order deg. rate TCE (ml m$^{-1}$ h$^{-1}$)</td>
<td>-</td>
<td>0.041</td>
<td>0.030</td>
<td>0.030</td>
</tr>
<tr>
<td>1st order deg. rate cis-DCE (ml m$^{-1}$ h$^{-1}$)</td>
<td>0.110</td>
<td>-</td>
<td>0.057</td>
<td>0.054</td>
</tr>
</tbody>
</table>

**MODEL ASSUMPTIONS AND RESULTS**

Existing models typically use only first order degradation rates with a constant rate coefficient and do not take competing reactions into account. A new modelling approach was therefore developed. The numerical model TBC (Transport, Biochemistry and Chemistry, Schäfer et al. (1998)) was upgraded to reproduce degradation of sorbed material and adsorption/desorption using Langmuir kinetics (Zepp & Wolfe, 1987):

\[
\frac{\partial C_{\text{mob}}}{\partial t} = (-k_{\text{sorb}}(1 - \Theta) R_i C_{\text{mob}} + k_{\text{desorb}} C_{\text{mat}}) \rho_{Fe} \frac{n_{\text{mat}}}{n_{\text{mob}}} \quad (1)
\]

\[
\frac{\partial C_{\text{mat}}}{\partial t} = (-k_{\text{sorb}}(1 - \Theta) R_i C_{\text{mob}} + k_{\text{desorb}} C_{\text{mat}}) - k_R C_{\text{mat}} \quad (2)
\]

The adsorption rate depends on a rate constant $k_{\text{sorb}}$, the fraction of sorptive sites occupied $\Theta$, the overall concentration of sorptive sites $R_i$ and the concentration of the chlorinated hydrocarbon in the mobile pore water, $C_{\text{mob}}$. The rate of desorption only depends on a rate constant $k_{\text{desorb}}$ and the concentration of the reactant adsorbed on the iron surface $C_{\text{mat}}$. The density of iron $\rho_{Fe}$, and the ratio of the porosities of matrix $n_{\text{mat}}$ and mobile pore water $n_{\text{mob}}$ are required for unit conversion. The degradation is realised by a first-order rate $k_R$ with respect to the adsorbed concentration $C_{\text{mat}}$. With this approach TBC is able to model competitive adsorption processes and mixed zero- and first-order degradation kinetics, as observed with high or low concentrations of chlorinated hydrocarbons respectively.

The reaction scheme (Fig. 1) assumed for the degradation of TCE was adopted from Arnold & Roberts (2000), which also provided adsorption and degradation rate constants that were transferred to our model. Thus it was possible to model the complete degradation pathway even though not all the metabolites were measured in our experiments. Note that the parameters in Arnold & Roberts (2000) were determined in batch experiments using pure electrolytic iron (Fisher) with a metal surface area/volume of solution ratio of 0.25 m$^2$ l$^{-1}$. In our column experiment a commercial iron with an iron content of 91% and a surface/volume ratio of 1510 m$^2$ l$^{-1}$ is used.

The best agreement between model results and measurements was obtained by increasing the degradation rates of the model by a factor of 80 and decreasing the adsorption coefficients by a factor of 27. Adsorption and degradation of contaminants...
can be scaled independently since pure adsorption depends on the surface structure of iron and the electrolyte composition, while pure degradation is related to electron transfer from iron to the adsorbed contaminant. The simulations were performed by assuming that the relative magnitudes of degradation rate constants and adsorption coefficients for all simulated contaminants are identical to the values determined by Arnold & Roberts (2000). This means the degradation rates of all substances are increased by the same factor and the adsorption coefficients for all species are decreased. At least three experiments: (a) only cis-DCE, (b) only TCE, and (c) a mixture of TCE and cis-DCE, are required to calibrate the model. The successful model calibration with a minimum of adjustments shows that the transfer of parameters obtained from batch experiments (Arnold & Roberts, 2000) to column experiments is possible, though there does not seem to be a simple linear dependency on the ratio of BET metal surface area vs volume of solution. The calibrated model allows calculation of the degradation of the single components at various concentrations as well as modelling the degradation of any mixtures of TCE and cis-DCE (e.g. Fig. 2).

CONCLUSIONS

By calibrating the TBC model parameters it was possible to obtain one single set of parameters that fits the measured concentration profiles of cis-DCE and TCE degradation as well as degradation of mixtures of both. The parameters provided by Arnold & Roberts (2000) allowed extrapolation of concentration profiles for metabolites not measured in our experiments. The calibrated model results, as well as the laboratory
measurements, show that TCE degradation is nearly unaffected by the presence of cis-DCE, while the degradation rate for cis-DCE decreases significantly upon addition of TCE. The model parameters indicate that TCE is more attracted to the reactive surface than cis-DCE. Hence, TCE is able to replace cis-DCE from the reactive surface, or the larger attraction of TCE prevents it from being dislodged. In contrast, cis-DCE can be replaced by TCE on the reactive surface, preventing its degradation, although the degradation of cis-DCE is faster than TCE.

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REFERENCES


