The opposing effects of bacterial activity and gas production on anaerobic TCE degradation in soil columns

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Abstract

This laboratory study explores the effect of growth substrate concentration on the anaerobic degradation of trichloroethylene (TCE) in sand packed columns. In all columns the growth substrate rapidly degraded to gas, that formed a separate phase. Biomass accumulated in the 0–4.8 cm section of the columns in proportion to the influent growth substrate concentration and biomass concentrations in the remaining sections of all columns were similar to the column receiving the lowest substrate concentration. Increases in growth substrate concentration up to 3030 mg-COD l⁻¹ promoted TCE degradation, but a further increase to 14300 mg-COD l⁻¹ reduced the amount of TCE completely dechlorinated but did not affect the production of chlorinated TCE intermediates. The mathematical model developed here satisfactorily described the enhancement in TCE dehalogenation for substrate concentration up to 3030 mg-COD l⁻¹; reproducing TCE dehalogenation for 14300 mg-COD l⁻¹ required that the moisture content used in simulation be lowered to 0.1. The study shows that volatilization of TCE can be significant and volatilization losses should be taken into account when anaerobic activity in in-situ bioremediation applications is stimulated via addition of growth substrates. An implication of the modeling simulations is that maintaining a lower, but uniform, substrate concentration over the contaminated region may lead to faster contaminant degradation.

Keywords: Chloroethenes; Dehalogenation; Modeling; Volatilisation; Computer simulation

1. Introduction

Chloroethenes, such as trichloroethylene (TCE), have been widely used as solvents and degreasing agents and are now among the most ubiquitous chlorinated contaminants found in the subsurface environment (Aulenta et al., 2005; Yeh et al., 2006). Pollution by these contaminants has attracted particular attention due to the potential for adverse effects following exposure (Adamson and Parkin, 2000). The possibility of lowering the cost of remediating chloroethene contaminated soils by stimulating anaerobic dechlorination activity has made it an attractive option (Adamson and Parkin, 2001). An often cited limitation of anaerobic transformations is the incomplete conversion of chlorinated compounds to intermediates, such as cis-1,2-dichloroethylene and vinyl chloride, which are more toxic than the parent chemicals (McCue et al., 2003). This concern has been partly addressed by studies that have shown complete anaerobic dehalogenation of chloroethenes to ethene by Dehalococcoides ethenogenes (Maymó-Gatell et al., 1997) and cultures of Clostridium species (Hata et al., 2004), or the complete degradation of chloroethenes by coupling anaerobic dehalogenation with oxidation by methanotrophic (El-Farhan et al., 2000; Tartakovský et al., 2005) and Fenton reactions (Chen et al., 2001; Watts and Teel, 2004).
However, the effect of anaerobic gases, such as methane, on the degradation of chlorinated chemicals has not been adequately explored in the literature. Methane has a solubility in water of 24.1 mg l⁻¹ at 25 °C and 101 kPa (Mackay and Shiu, 1974) and active biodegradation can cause methane concentration to exceed the solubility limit and form a gaseous phase into which chloroethenes may volatilize from the aqueous phase (Van Breukelen et al., 2003; Mulligan and Yong, 2004; Amos et al., 2005). As the chemicals volatilizing into the gaseous phase do not undergo degradation, the overall amount of the chlorinated compounds degraded in the subsurface environment can decrease. Furthermore, contaminant biodegradation may also be impacted by a separate gas phase occupying a part of the pore space and reducing the hydraulic conductivity of soil (Islam and Singhal, 2004; Fortuin and Willemse, 2005; Singhal and Islam, Submitted for publication). This can lead to formation of preferential flow paths so that the contaminant plume circumvents areas of active biological activity, thereby decreasing the amount of contaminant biodegraded in the field.

Bioremediation applications generally involve enhancing biological activity via addition of growth substrates. As indicated previously, this practice can have two counteracting effects – on the one hand increased bioactivity can enhance the degradation of dissolved volatile chloroethenes, while on the other hand an increase in volatilisation due to greater methane production may decrease the amount of contaminant degraded. Mathematical models used to design such applications evaluate the effect of different controls and operating conditions (e.g., locations and numbers of injection wells, concentrations in feed, injection and pumping rates, etc.), but generally ignore the effects of gas production on bioremediation efficiency or assume instantaneous degassing (e.g., Van Breukelen et al., 2004). These assumptions can compromise the efficacy of proposed treatment by introducing errors of unknown magnitudes. This work investigates the effects of gas production on TCE degradation in anaerobic sand columns using a combination of laboratory experiments and mathematical modeling.

### 2. Materials and methods

Laboratory experiments were conducted using five columns packed with coarse sand (ASTM C-190), previously incinerated at 550 °C, and operated in an upflow mode. Columns were made from 5.8 cm internal and 7.7 cm external diameter PVC tubing 61 cm long with 10 sampling ports. At startup the columns were saturated with deaerated deionized water and fed a medium containing (per liter of deionised water): methanol, 1.58 g; sodium formate, 1.6 g; yeast extract, 0.1 g; Na₂S, 0.2 g; trace metal solution (consisting of nitric acid, 4.5 g; FeCl₃·4H₂O, 0.4 g; MnCl₂·4H₂O, 0.1 g; CoCl₂·6H₂O, 0.17 g; ZnCl₂, 0.1 g; CaCl₂, 0.2 g; H₂BO₃, 0.019 g; and sodium molybdate, 0.01 g and adjusted to a pH of 7 with KOH), 9 ml; vitamin solution (consisting of biotin, 0.002 g; folic acid, 0.002 g; pyridoxine hydrochloride, 0.01 g; thiamine hydrochloride, 0.005 g; riboflavin, 0.005 g; nicotinic acid, 0.005 g; pantothenic acid 0.005 g; B₁₂, 0.0001 g; p-aminobenzoic acid, 0.005 g; thioctic acid, 0.005 g; K₂HPO₄, 2.22 g; K₃PO₄, 1.50 g; NH₄Cl, 0.50 g and MgCl₂, 0.17 g. The columns were then inoculated with an anaerobic bacterial culture, previously collected from a local wastewater treatment plant and acclimated to TCE. All columns were provided media from a common reservoir, which was continuously purged with a gas consisting of 10% H₂, 5% CO₂, and 85% N₂. A liquid flow rate of 2 ml h⁻¹ was maintained in each column using a peristaltic pump. The growth substrate (a mix of methanol and sodium formate) and TCE was injected using a syringe pump into the column inflow. The eluent from each column was collected in separate glass bottles, which was periodically purged with nitrogen to transfer the eluting chloroethenes to the attached Vocarb 4000 traps. As shown on Fig. 1, one of the five columns (Column 5) was scanned using a dual source (450 mCi of ²⁴²Am and 300 mCi of ¹³³Cs) gamma unit to quantify biomass and biogas buildup in the column. Details of gamma ray system are discussed by Ferrand et al. (1986). However, the biomass showed an insignificant attenuation of gamma beams and both sources only served to provide independent measurements of gas accumulation in the column.

### Fig. 1. Schematic layout of column setup.
The columns were operated for one year under different conditions until steady state performance was achieved. This paper focuses on the observed degradation of TCE in the last two months of the study, after which the columns were dismantled. In the immediately preceding phase all columns were operated in a likewise manner and comparable removal efficiencies for TCE removal were observed in all columns, indicating that similar initial conditions prevailed in all columns. During this phase the influent TCE concentration was approximately 64.5 mg l$^{-1}$ and the composition of media used is presented in Table 1. The following process variables were quantified: TCE and its daughter products (chloroethane, 1,1 dichloroethane, 1,2 dichloroethene, 1,1 dichloroethylene, 1,2 dichloroethylene, vinyl chloride), methanol, sodium formate, acetate, propionate, n-butyr at, methane, carbon dioxide, overall substrate concentration as COD, and biomass.

The concentrations of TCE and its daughter products dissolved in the inflow and outflow were quantified using gas chromatograph (HP Model 5840 A) equipped with a purge and trap sampler (Tekmar LSC2) and an electrolytic conductivity detector (OI Corporation). The analytical column was 2.4 m × 3.1 mm SS with 1% SP1000 on 60/80 Carbopack B (Supelco Inc.) kept at 45 °C for the initial 3 min, followed by 8 °C min$^{-1}$ rise to 220 °C and a final hold of 15 min, with helium as the carrier gas at 40 ml min$^{-1}$.

Methanol was quantified using a gas chromatograph (Sigma 2000 GC) equipped with a 30 m × 0.53 mm ID SPB-1 fused silica capillary column connected to a flame ionisation detector using 2 ml min$^{-1}$ of helium as the carrier gas. The column temperature was 50 °C for first 3 min followed by 25 °C min$^{-1}$ rise to 160 °C and a 2 min final hold. Analysis for volatile fatty acids involved an initial extraction from water to ethyl ether followed by an injection of the ether onto a 1.8 m × 6.4 mm SS column packed with 15% SP1220/1% H$_3$PO$_4$ on 100/120 Chromosorb WAW (Supelco Inc.) connected to a Hot Wire Detector (Sigma 2000 GC). The column was operated isothermally at 130 °C with helium as the carrier gas at a flow rate of 85 ml min$^{-1}$. The organic concentration was measured as COD using high range vials (HACH). Methane and carbon dioxide were measured using a 2.4 m × 3.2 mm SS column packed with Haysep-Q 80/100 mesh (Alltech Associates) connected to the Hot Wire Detector. The column was operated isothermally at 50 °C with helium as the carrier gas at a flow rate of 30 ml min$^{-1}$.

The suspended and sand-attached biomass were quantified as protein. After the columns were dismantled, sand samples were collected in 2.4 cm increments from the inlet to the first sampling port and in 4.8 cm increments thereafter. The attached biomass was sheared from the sand grains into an aqueous solution using a Homogenizer (The Virtis Company) and the protein from the biomass in solution was extracted by adding 1 ml of 1 M sodium hydroxide to solution. For aqueous samples collected directly from the columns, 1 ml of 1 M sodium hydroxide was added to the cell pellet obtained by centrifuging. The extracted protein was analysed using the Biorad Protein Assay Kit I (Biorad).

### 3. Experimental findings

#### 3.1. Biogas production

The gas buildup in the column in the early stages of the study was determined using a low energy americium and a high energy caesium source. The first scan of the column, performed shortly after bacterial inoculation of the columns, using americium showed gas saturations of 3–9% along the column over the two days it took to scan the column. The following scan, started immediately after the americium scan, with caesium gave similar values, except for an increase in gas saturation in the inlet region (0–2.5 cm section) from 6% to 11%. Subsequent scans showed that gas saturation in the inlet region increased to 17% by day nine and then remained relatively unaffected, and the saturations in the remainder of the column showed little variation. The rates of biogas production in the columns are presented in Fig. 2a, which shows that methane and carbon dioxide production increased for larger influent substrate concentrations.

#### 3.2. Biomass buildup

For influent substrate concentrations up to 821 mg l$^{-1}$ the attached biomass concentrations were similar (0.17–0.27 mg kg$^{-1}$) in all columns. For influent COD concentrations of 3032 mg l$^{-1}$ and 14294 mg l$^{-1}$ the attached biomass concentrations were 1.5 g kg$^{-1}$ and 5.3 g kg$^{-1}$ in the 0–2.4 cm section and 0.46 g kg$^{-1}$ and 1.0 g kg$^{-1}$ in the 2.4–4.8 cm section, respectively, and values in the remaining sections were similar to those observed for columns receiving the lower substrate concentrations. The eluting suspended biomass concentrations were similar, ranging from 0.19 to 0.22 g-protein l$^{-1}$. These observations indicate that microbial activity, and therefore biogas production and TCE biodegradation, is primarily occurring in the column inlet region.

#### 3.3. Substrate degradation

The influent methanol and sodium formate concentrations and the associated COD values for the columns are given in Table 1. The growth substrates degraded rapidly,

### Table 1

<table>
<thead>
<tr>
<th>Column no.</th>
<th>Methanol (g l$^{-1}$)</th>
<th>Sodium formate (g l$^{-1}$)</th>
<th>COD$_{in}$ ± Std. Dev. (mg l$^{-1}$)</th>
<th>COD$_{eff}$ ± Std. Dev. (mg l$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.008</td>
<td>0.008</td>
<td>492 ± 10</td>
<td>383 ± 16</td>
</tr>
<tr>
<td>2</td>
<td>0.04</td>
<td>0.04</td>
<td>550 ± 12</td>
<td>395 ± 23</td>
</tr>
<tr>
<td>3</td>
<td>0.4</td>
<td>0.4</td>
<td>821 ± 128</td>
<td>650 ± 37</td>
</tr>
<tr>
<td>4</td>
<td>1.6</td>
<td>1.6</td>
<td>3030 ± 163</td>
<td>1070 ± 44</td>
</tr>
<tr>
<td>5</td>
<td>7.9</td>
<td>8</td>
<td>14300 ± 300</td>
<td>4630 ± 240</td>
</tr>
</tbody>
</table>
with no methanol and sodium formate detected in the first sampling, except in Column 5 where trace amounts (<1 mg l\(^{-1}\)) of methanol were detected. The amount of COD eluting increased for higher influent COD, suggesting that some organic matter eluted from the columns. The composition of the effluent COD could not be determined, but as no growth substrates or intermediate fatty acids were detected in the sampling ports and no attached biomass growth occurred beyond the first few centimeters in the columns, the effluent COD values likely reflect a combination of decaying biomass and the reductant Na\(_2\)S used to lower the redox potential of the media. The change in pH resulting from substrate degradation was small with influent pH of 6.8 changing to effluent pHs of 6.58, 6.53, 6.55, 6.64, and 7.31, respectively, for Columns 1–5.

### 3.4. TCE degradation

TCE degradation in the columns gave the following daughter products: chloroethane, 1,1-dichloroethylene, 1,2-dichloroethylene, and vinyl chloride in the molar ratio 15:1:18:30:15:263. The total TCE degraded was expressed as the chloride ions released during TCE dechlorination. This involved summing the concentrations of chloride ions released by the conversion of TCE to the various daughter products (for example, conversion of one mol of TCE to chloroethane release two mol of chloride ions). Complete dechlorination of TCE yielded a non-chlorinated endproduct (e.g., ethylene), which was not measured and had to be estimated as the difference of moles of TCE degraded (i.e., the influent minus the effluent TCE concentration) and total moles of daughter products produced in the columns. The fraction of TCE degraded was expressed as the ratio of total chloride ions released during TCE dehalogenation and the chloride ions corresponding to the influent TCE concentration. The fraction of TCE lost via leakage from the columns was estimated by separately operating a microbiologically inert column. As TCE loss in this microbially inert column only ranged from 2.5% to 4.5%, with an average of 3%, the observed TCE disappearance is attributed to its conversion to intermediates or the endproduct. The fraction of TCE degraded in the columns is shown on Fig. 2b. The data show that increasing the growth substrate concentration from 492 mg-COD l\(^{-1}\) to 821 mg-COD l\(^{-1}\) had little effect on TCE degradation, which remained at approximately 10%, while increasing the substrate concentration to 3030 mg-COD l\(^{-1}\) enhanced the TCE degraded to approximately 22%, but further increasing the substrate to 14300 mg-COD l\(^{-1}\) lowered the TCE degraded to approximately 11%. The conversion of TCE to its chlorinated intermediates was enhanced, or unaffected, by an increase in growth substrate; however, further degradation of chlorinated intermediates to non-chlorinated endproduct increased from ≈8% to 15% when the growth substrate concentration was changed from 492 to 3030 mg-COD l\(^{-1}\), but then decreased to 4% when the substrate was further increased to 14300 mg-COD l\(^{-1}\). These observations indicate that high substrate concentrations promote the conversion of TCE to its less-chlorinated daughter products, but substrate concentrations above a certain optimal value can lower the conversion of the chlorinated intermediates to the non-chlorinated endproduct.

### 4. Model development

#### 4.1. TCE degradation

The two modeling approaches commonly used for packed reactors involve the use of advection-dispersion processes and systems of tanks-in-series (Hermanowicz and Ganczarczyk, 1985). This tanks-in-series approach is better able to accommodate coarsely discretised data and has the added advantage of yielding algebraic equations for process variables at steady state. In this paper a tanks-in-series model is presented for the anaerobic degradation of chlorinated compounds in a continuous flow bioreactor that accounts for substrate uptake, biomass development,
biomass transport, gas formation, partitioning of volatile compounds into the gas phase, and dechlorination of dissolved chlorinated chemicals.

The column was divided into twelve completely mixed reactors, connected in series, and mass balance equations are written for each reactor. The effluent substrate and biomass concentrations are assumed to be the same as that in solution. The biomass is divided into attached and suspended biomass fractions, which are assumed to contain active and non-active bacterial populations. The active biomass is assumed to produce new biomass as well as undergo decay and cell lysis, while the non-active cells only undergo decay and cell lysis. Expressing the attached biomass, for convenience, as equivalent suspended biomass, yields the following mass balance equations:

Substrate:

\[
\left( \frac{V_w}{dt} \right)^i = Q_w S_i - Q_w S^{i-1} - \frac{V_w \mu X^{i'}}{Y_{s/s}}
\]

Active Biomass:

\[
\left( \frac{V_w}{dt} \right)^i = Q_w X^{i-1} - Q_w f_i^{a} X^{i'} + V_w \mu X^{i'} - V_w b X^{i'}
\]

Non-active Biomass:

\[
\left( \frac{V_w}{dt} \right)^i = Q_w X^{i-1} - Q_w f_i^{a} X^{i'} + V_w b X^{i'} - V_w b X^{i'}
\]

where, \(\mu\) = biomass specific growth rate; \(b\) = biomass decay rate; \(f_i^{a}\), \(f_i^{n}\) = fraction of non-active and active biomass leaving reactor; \(Q_w\) = water flow rate; \(S\) = substrate concentration; \(X^{a}\), \(X^{n}\) = non-active and active biomass concentration; \(V_w\) = volume of liquid phase in the reactor (=total pore volume of the column-section * water saturation); \(Y_{s/s}\) = yield for biomass formation from substrate; and superscripts \(i-1\) and \(i\) denote the concentration entering and that in reactor \(i\).

Expressing the specific growth rate as a first order function of the substrate concentration (i.e., \(\mu = \mu_{\text{max}} S\)), the steady state substrate concentration can be obtained by solving:

\[
\mu_{\text{max}} Y_{s/s} \theta' (S')^2 - (Y_{s/s} (\mu_{\text{max}} S^{-1} \theta' + f_i^{a} + b \theta')) + \mu_{\text{max}} Y_{s/s} \theta' S' + Y_{s/s} (f_i^{a} + b \theta') S'^{-1} = 0
\]

where, \(\theta = V_w / Q_w\) = hydraulic retention time of water in the reactor.

The corresponding active and non-active biomass concentrations are obtained as:

\[
X^{a'} = \frac{X^{a'} - Y_{s/s} (S^{-1} - S')}{f_i^{a} + b \theta'}
\]

\[
X^{n'} = \frac{b \theta' X^{n'}}{b \theta' + f_i^{n}}
\]

Mass balance equations for TCE in the liquid and gas phases, as follows:

\[
\left( \frac{V_w}{dt} \right)^i = Q_w TCE^{i-1} - Q_w TCE^{i'} - V_w r_{\text{TCE}} TCE^{i'} + I_g
\]

\[
\left( \frac{V_g}{dt} \right)^i = Q_g TCE^{i-1} - (Q_g TCE^{i'} + \Delta Q_g TCE^{i'}) - I_g
\]

where, \(I_g\) = mass rate of TCE transferred from the gas phase to liquid phase; \(Q_g\) = gas flow rate; \(\Delta Q_g\) = gas produced in reactor; \(r_{\text{TCE}}\) = rate of TCE degradation in water phase; \(TCE^{i-1}_g\), \(TCE^{i-1}_w\) = TCE concentration in the gas and water phases; and, \(V_g\) = volume of gas phase.

If the TCE concentrations in gas and water phases are assumed to be in equilibrium, then:

\[
TCE^{i}_w = \frac{Q_w TCE^{i-1} + Q_g TCE^{i-1}}{Q_w + V_w r_{\text{TCE}} + H (Q_g + \Delta Q_g)}
\]

\[
TCE^{i}_g = H TCE^{i}_w
\]

where, \(H\) = Henry’s constant for TCE.

4.2. Gas phase formation

The gas phase is assumed to only consist of methane and carbon dioxide. Once methane exceeds its solubility in water and forms a separate gas phase, carbon dioxide distributes between the gas phase and its aqueous forms (dissolved carbon dioxide, bicarbonate, and carbonate ions), adding to the volume of the gaseous phase. For reactor \(i\) the gas generated may be described by:

\[
\Delta Q_g = \Delta Q_{\text{CH}_4} + \Delta Q_{\text{CO}_2}
\]

where, \(\Delta Q_{\text{CH}_4}, \Delta Q_{\text{CO}_2}\) = contribution by methane and carbon dioxide to the gas produced in reactor.

The amount of separate phase methane produced in any reactor, \(\Delta Q_{\text{CH}_4}\), is the difference of rate of methane production and the amount advected in water from the reactor. Methane is assumed to form a gaseous phase only when the rate of production exceeds the maximum advective capacity of water for methane, defined as the product of flow rate and methane solubility in water. Thus, the amount of methane produced per unit time can be estimated as

\[
\Delta Q_{\text{CH}_4} = \text{Max} \left( 0, Y_{\text{CH}_4/s} \mu_{\text{max}} X^{a'} S^{i'} - Q_w (\text{CH}_{4,\text{sat}} - \text{CH}_{4}^{i}) \right) \frac{RT \theta}{P}
\]

where, \(\text{CH}_{4,\text{sat}}\) = concentration of dissolved methane; \(\text{CH}_{4,\text{sat}}\) = concentration of methane in water at saturation (24.1 mg l\(^{-1}\) at 25 °C and 101 kPa) (Mackay and Shiu, 1974); \(P\) = total pressure of the gas phase (assumed to equal 101 kPa); \(R\) = universal gas constant (8.314 k J k\(^{-1}\) mol\(^{-1}\)); \(T\) = absolute temperature of gas phase (approximately 20 °C in the present study); and, \(Y_{\text{CH}_4/s}\) = yield of methane (mmol) per unit substrate (mg-COD) degraded.
The amount of carbon dioxide distributing between the gaseous and liquid phases, assuming equilibrium, is controlled by the partial pressure of carbon dioxide in the gas phase, which can be estimated as

\[
p_{i}^{\text{CO}_2} = \frac{n_{i}^{\text{CO}_2} P}{n_{\text{CH}_4} + n_{i}^{\text{CO}_2}} = \frac{Q_{i}^{\text{CO}_2} P}{Q_{\text{CO}_2} + Q_{\text{CH}_4}}
\]

(13)

where, \(n_{\text{CH}_4}, n_{i}^{\text{CO}_2}\) are moles of methane and carbon dioxide in the gas phase and \(p_{i}^{\text{CO}_2}\) is partial pressure of carbon dioxide in the ith reactor.

At equilibrium, the concentration of \(\text{H}_2\text{CO}_3\) (hydrated carbon dioxide plus carbonic acid) and \(p_{\text{CO}_2}\) are related by the equilibrium constant \(K_{1}\) (10^{-1.41} at 20 °C), bicarbonate and \(\text{H}_2\text{CO}_3\) are related by the first dissociation constant for carbonic acid (\(K_{a,1} = 10^{-6.38}\) at 20 °C), and carbonate and bicarbonate are related by the second dissociation constant for carbonic acid (\(K_{a,2} = 10^{-10.38}\) at 20 °C) (Snoeyink and Jenkins, 1980). The total carbonate species in solution (\(\text{CO}_3\) and \(\text{H}_2\text{CO}_3\)) can therefore be written as

\[
C_{i}^{\text{CO}_3} = K_{1}p_{i}^{\text{CO}_2} \left( 1 + \frac{K_{a,1} K_{a,2}}{[\text{H}^+]^2} \right)
\]

(14)

where, \([\text{H}^+]\) defines hydrogen ion concentration. The change in the volume of gas phase due to addition of carbon dioxide is then calculated using mass balance as the difference of the moles of CO$_2$ produced per unit time and the change in the flux of the liquid phase carbonate species, as follows:

\[
\Delta Q_{i}^{\text{CO}_2} = Y_{\text{CO}_2/s} \left( \frac{\mu_{\text{max}}}{Y_{s/\text{a}}} X S Y_{i} - Q_{i}^{\text{CO}_2} \Delta C_{i}^{\text{CO}_3} \right) \frac{RTQ_{i}}{P}
\]

(15)

where, \(C_{i}^{\text{CO}_3}\) is total dissolved carbonate concentration and \(Y_{\text{CO}_2/s}\) is yield of carbon dioxide (mmol) per unit substrate (mg-COD) degraded.

4.3. Water content

The water content in the columns was estimated assuming a uniform and continuous gas production in the columns. Although gas release from the columns occurred in periodic pulses, this assumption was necessary to simplify the procedure for estimating the gas and water content in a reactor using the generalised Darcy’s Law (Huyakorn and Pinder, 1983):

\[
q_{a} = \frac{k_{s} k_{r_a}}{\mu_{s}} \left( \frac{d p_{s}}{d Z} + \rho_{s} g \right)
\]

(16)

where, \(\mu_{s}\) is dynamic viscosity; \(\rho_{s}\) is density; \(g\) is acceleration due to gravity; \(k_{r}\) is intrinsic permeability of the medium; \(k_{s}\) is relative permeability; \(d p_{s}/d Z\) is pressure gradient in the vertically upward flow direction; \(q_{a}\) is Darcy flux; and, \(a = \text{air (a) or water (w)}\) phase.

It is further assumed that the water content in any column can be approximated by a single value. The assumption is justified on the basis of observations that change in gas saturation are small (observed to vary between 5% and 14% of porosity for influent COD of 3030 mg l^{-1}) and the large changes are limited to the inlet region of the columns. Therefore, the derivative of the capillary pressure with respect to the vertical direction is zero, giving:

\[
\frac{\mu_{w} q_{a}}{k_{rw}} - \frac{\mu_{a} q_{a}}{k_{ra}} + k_{s} (\rho_{w} - \rho_{a}) = 0
\]

(17)

The intrinsic permeability is (Huyakorn and Pinder, 1983):

\[
K_{s} = \frac{\rho_{w} \varepsilon_{w} k_{rs}}{\rho_{a} q_{a}} = K_{r_a \varepsilon_{r_a}}
\]

(18)

where, \(K_{s}\) is hydraulic conductivity and \(K_{r_a}\) is saturated hydraulic conductivity. The relative permeability of water \((k_{rw})\) and air \((k_{ra})\) are given as (Parker et al., 1987; Parker, 1989):

\[
k_{r_a} (\theta_{w}) = \theta_{e}^{1/2} \left( 1 - (1 - \theta_{e}^{1/2} m^{2})^{2} \right)
\]

(19)

\[
k_{rw} (\theta_{w}) = (1 - \theta_{e})^{1/2} (1 - \theta_{e}^{1/2} m^{2})
\]

(20)

where, \(\theta_{e}\) is normalised water content \((\theta_{e} = (\theta_{a} - \theta_{wr})/ (\theta_{a} - \theta_{wr})); \theta_{w}\) is water content; \(\theta_{wr}\) is residual water content; \(\theta_{ws}\) is saturated water content; \(m = 1 - 1/n\); and, \(n = \text{van Genuchten} \) equation parameter.

5. Model calibration

5.1. Parameter estimation

Values for \(K_{i/\text{a}}, \theta_{\text{wr}}, \) and \(n\) for the sand used were previously estimated as 0.281 cm s^{-1}, 0.024 and 7.65 (Cho and Jaffé, 1993). The saturated water content is approximated as equaling the average porosity measured using the gamma setup, 0.306 (Singhal, 1995). Substituting these values along with the gas flow rates (Fig. 2a) into Eqs. (17)–(20), and solving the equations using the Levenberg Marquardt algorithm, LMDIFF (Morris, 1993) to minimize the square of the difference between the observed and predicted attached biomass concentrations gave a maximum substrate
degradation rate of 0.39 l mg⁻¹ d⁻¹. The shearing of sand-attached biomass is affected by the microbial growth rate (e.g., Rittmann, 1982; Taylor and Jaffe, 1990). Also, in the current experiments it was observed that biomass in suspension did not significantly reattach to sand, probably because regions devoid of organic substrate result in microbial starvation which promotes detachment (Allison et al., 1998). Accordingly, the biomass in the effluent was expressed as a function of the substrate degradation rate and the concentration of biomass suspended in the inflow to the reactor, yielding the following approximate relationship:

\[ X_{v_{eff}} = 3.9 \times 10^{-6} \left( \Delta S - \frac{\Delta X}{\Delta t} \right) + X_{v_{eff}}^{1-1} \]  

Where, \( \Delta S = \) substrate degraded in the reactor and \( X_{v_{eff}} = \) suspended biomass concentration in the effluent. From Eqs. (2), (3) and (21), \( f_v = X_{v_{eff}}/X_v \). The fraction of nonactive biomass leaving, \( f_v^L \), was assumed to be of the same order as \( f_v \).

The TCE degradation rate was modelled using the following relationship obtained from batch experiments (Singhal, 1995):

\[ r_{TCE_{v}} = \frac{\partial TCE}{\partial t} = 0.089X_v. \]  

5.2. Simulations

Methane and carbon dioxide (Fig. 2a) are fit well by the model with respective maximum absolute errors of 0.4 mmol d⁻¹ and 0.5 mmol d⁻¹ compared to peak production rates of 7.0 and 5.5 for methane and carbon dioxide. The model also gave good fits to the attached biomass with maximum absolute error <0.2 g kg⁻¹ (predictions are not presented here) and growth substrate concentrations with the predicted and observed substrate being completely degraded in the first few centimeters of the columns. For TCE degradation, the model gave good fits to the observed TCE degradation (solid line and hollow-square symbols in Fig. 2c) for low to intermediate influent substrate concentration, but failed to show the decrease in TCE degradation at the 14300 mg-COD l⁻¹ substrate concentration. Simulations suggest that the majority (65–90%) of the biomass is actively degrading TCE, even in regions devoid of substrate. The efflux of TCE (as a percentage of the influent TCE flux) in the water and gas phases for smallest to largest influent growth substrate concentrations were 93% and 1.6%, 92% and 2.2%, 87% and 4.5%, 52% and 22%, and 20% and 40%, respectively. As expected, TCE volatilization is enhanced by an increase in gas production. A simulation of the column receiving 14300 mg-COD l⁻¹ in the absence of any volatilization losses shows that TCE degradation of 75% can be expected, indicating that ignoring volatilization losses can lead to grossly overpredicting the amount of TCE degraded.

The lack of fit between the model-predicted and observed TCE degradation at high gas flows is attributed to the simplistic modelling of gas flow and its effect on water content and TCE degradation in the columns. Increasing the growth substrate concentration from 3030 mg l⁻¹ to 14300 mg l⁻¹ enhanced methane production from 1.2 mmol d⁻¹ to 7 mmol d⁻¹, but the model estimates a change of only 0.29 to 0.28, respectively. This behaviour is an artifact of the assumption that the capillary pressure is constant within the entire column; the deviations between the prevailing and assumed capillary pressures are exacerbated by the compression of gas at higher gas flow rates. Accordingly, the prevailing water content in the columns can be expected to be lower than that predicted. To test the effect of lower water contents on TCE degradation simulations were done with lower moisture content for the column receiving 14300 mg-COD l⁻¹. Reducing the water content to less than 0.18 led to a reduction in the TCE dechlorinated compared to that in the column receiving 3030 mg-COD l⁻¹, and further lowering the moisture content to 0.10 (i.e., a gas saturation of 67%) gave a reasonable fit to the observed TCE degradation at the highest substrate concentration (shown as a dashed line in Fig. 2c). Incorporating a more sophisticated description on the effect of gas flow on the water content will give a better fit to the observed TCE degradation at high growth substrate concentrations.

6. Conclusions

This study shows that biogas production is likely to have a significant effect on the degradation of volatile chemicals, such as TCE, in anaerobic environments. Increasing substrate concentrations does not necessarily lead to greater TCE degradation. In fact, increasing substrate concentration beyond certain values will have a negative impact on complete TCE dehalogenation, although the conversion of TCE to its chlorinated daughter products may remain unchanged, or even be enhanced. Modelling simulations suggest that suspended biomass can lead to populations of active biomass in regions containing no growth substrates.

The main implication of the study is that biogas transport is an important phenomena that needs to be considered during in-situ bioremediation of volatile contaminants. A corollary to this conclusion is that maintaining lower, but uniform, concentration of substrate in the contaminated soil is likely to result in greater degradation of volatile contaminants.

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