Remediation of soil and groundwater
Rizlan Bernier-Latmani
Problem set # 4: vapor phase processes
Solution

Problem 1:

$Q = 0.3\ m^3/h$
$C_i = 560\ \mu g/L$ air
$h=1$ m
$V = ?$
$k=120.3$ mg toluene/g cell/min
$K_S=17.4$ mg/L air
Initial biomass X= 1 g cells/L (expressed as a function of volume of air flow not volume of bed)
This is intended to be the biomass concentration that is present at the operational state of the biofilter.

Monod model for growth:

$$\frac{dC}{dt} = -\frac{kX}{C + K_s}C$$

We assume that X is constant (equal growth and death of microorganisms) and we see that $C_i << K_S$
Hence, the equation simplifies to:

$$\frac{dC}{dt} = -\frac{kX}{K_s}C$$

Which corresponds to first order kinetics:

$$C_{out} = C_{in}e^{-\frac{kX}{K_s}t} = C_{in}e^{-k't}$$

We can calculate k':

$$k' = \frac{kX}{K_s} = \frac{120.3\frac{mg_{toluene}}{g_{cell}min} * 1\frac{g_{cell}}{L}}{17.4\frac{mg_{toluene}}{L}} = 6.91\ minutes^{-1}$$

We are missing t, the residence time of air in the reactor (called EBCT):

$$EBCT = \frac{V}{Q} = \frac{\pi r^2 h}{Q}$$

We don't have the radius of the biofilter, let's do a sensitivity analysis to determine how the effluent concentration depends on the biofilter diameter:

$$C_{out} = C_{in}e^{-k'EBCT} = C_{in}e^{-k'\frac{\pi r^2 h}{Q}}$$

We calculate:

d (cm)	3	6	8	10	20	30
C (µg/L)	210.7	11.2	0.54	0.01	7.6e-17	2.0e-40
EBCT (min)	0.14	0.56	1	1.57	6.3	14.1

Clearly, the larger the diameter, the more removal. However, the residence time in the biofilter becomes too high when the diameter exceeds 20 cm and the removal may not be sufficient if the diameter is below 8 cm.

Problem 2:

Air stripper to remove ethylbenzene.

What is the height of the air stripping column?
Z = NTU*HTU → Need to calculate HTU and NTU

column diameter = 0.915 m
packing = 25 mm Rachig rings => α=330 and n=0.22
$D_L = 6*10^{-6}$ cm^2/s
air: water ratio=100:1 → Q_A/Q_W=100

First HTU,

$$HTU = \frac{L}{M_w K_L a}$$

We need L:

$$L = \frac{Q\rho_L}{S} = \frac{643.45 \frac{L}{min}\ 998.2 \frac{kg}{m^3} \frac{1m^3}{1000L}}{\pi\left(\frac{0.915}{2}\right)^2 m^2} = 976.8 \frac{kg}{m^2.min} = 16.3 \frac{kg}{m^2.s}$$

And K_La:

$$K_L a = \alpha\, D_L \left(\frac{L}{\mu_L}\right)^{1-n} \left(\frac{\mu_L}{\rho_L D_L}\right)^{0.5}$$

$$D_L = 6 * 10^{-6} \frac{cm^2}{s} * \frac{1m^2}{10^4 cm^2} = 6 * 10^{-10} \frac{m^2}{s}$$

$\mu_L = 1.002*10^{-3}$ kg/m.s
$\rho_L = 998.2$ kg/m^3

$$K_L a = 330 * 6 * 10^{-10} \frac{m^2}{s} * \left(\frac{16.3 \frac{kg}{m^2 * s}}{1.002 * 10^{-3} \frac{kg}{m.s}}\right)^{0.78} \left(\frac{1.002 * 10^{-3} \frac{kg}{m.s}}{998.2 \frac{kg}{m^3} * 6 * 10^{-10} \frac{m^2}{s}}\right)^{0.5} = 0.016\ s^{-1}$$

So the height of one transfer unit is:

$$HTU = \frac{904\,\frac{mol}{m^2 * s}}{55{,}600\,\frac{mol}{m^3} * 0.016\,s^{-1}} = 1.04m$$

Next NTU,

$$NTU = \left(\frac{R}{R-1}\right)\ln\left(\frac{\left(\frac{C_i}{C_0}\right)(R-1)+1}{R}\right)$$

$$R = K'_H\left(\frac{Q_A}{Q_W}\right) = 0.27 * 100 = 27\ [-]$$

C_i = 1'000 µg/L
C_0 = 35 µg/L

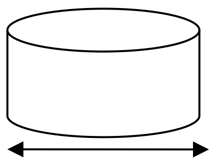
The number of transfer unit is: NTU=3.44

Finally, the height,

Z = NTU * HTU = 1.04 * 3.44 = 3.6 m

The tower is 3.6 m tall

Problem 3:



$V_{TCA} = 10\text{m}^3$ $\rho_{wb} = 2'090\ \text{kg/m}^3$
$P_V = 0.13$ atm $K_D = 10^{-5}\ \text{m}^3/\text{g}$
$M_W = 133.4$ g/mol $\theta = 0.10\ \text{m}^3/\text{m}^3$
$\rho_{TCA} = 1'325\ \text{kg/m}^3$ $\varepsilon = 0.25$
$K'_H = 0.56$ $T_{soil} = 20°\text{C}$
$K_{OW} = 10^{-2.5}$ $\rho_{air} = 1.28\ \text{kg/m}^3$

Time to remove 95% TCA with SVE

$$Q = 3\ \text{m}^3/\text{min}$$

$$m_{TCA,tot} = \rho_{TCA} \cdot V_{TCA} = 1'325\ \text{kg/m}^3 \cdot 10\text{m}^3 = \underline{13'250\ \text{kg}}$$

Bulk density of the soil ρ_b

$$M_{soil,tot} = M_S + M_G + M_L$$

$$\rho_{wb} \cdot V_T = \rho_b V_T + \rho_{air} V_G + \rho_w V_L$$

$$= \rho_b V_T + \theta \rho_w V_T + (\varepsilon - \theta)\rho_{air} V_T$$

$$\left(because\ \theta = \frac{V_L}{V_T}\right) \qquad \left(because\ \left(\underbrace{\frac{V_L+V_G}{V_T}}_{\varepsilon} - \underbrace{\frac{V_L}{V_T}}_{\theta}\right)\rho_{air} \cdot V_T = \rho_{air} V_G\right)$$

$$\Rightarrow \ \rho_{wb} V_T = V_T(\rho_b + \theta\rho_w + (\varepsilon - \theta)\rho_{air})$$

$$\Rightarrow \ \rho_{wb} = \rho_b + \theta\rho_w + (\varepsilon - \theta)\rho_{air} \ \Rightarrow \ \rho_b = \rho_{wb} - \theta\rho_w - \rho_{air}(\varepsilon - \theta)$$

$$\rho_b = 2'090\,\frac{\text{kg}}{\text{m}^3} - 0.10\,\frac{\text{m}^3}{\text{m}^3} \cdot 1'000\,\frac{\text{kg}}{\text{m}^3} - 1.28\,\frac{\text{kg}}{\text{m}^3}(0.15)$$

$$\underline{\rho_b = 1'989.8\ \frac{\text{kg}}{\text{m}^3}}$$

Calculate volume of soil contaminated

$$V_T = \pi r^2 \text{H} = \pi \cdot (15)^2 \cdot 8 = \underline{5'655 m^3}$$

<u>Initial distribution of TCA</u>

$$m_{TCA,tot} = m_{TCA,s} + m_{TCA,aq} + m_{TCA,g}$$
$$= C_{TCA,s} M_S + C_{TCA,aq} V_L + C_{TCA,g} V_G$$
$$= K_D M_S C_{TCA,aq} + C_{TCA,aq} V_L + K_H' C_{TCA,aq} V_G$$

$$\Rightarrow C_{TCA,aq} = \frac{m_{TCA,tot}}{K_D M_S + V_L + K_H' V_G}$$

$$M_S = \rho_b V_T$$
$$V_L = V_T \theta$$
$$V_G = (\varepsilon - \theta) V_T$$

$$= \frac{m_{TCA,tot}}{K_D \rho_b V_T + \theta V_T + K_H'(\varepsilon - \theta) V_T}$$

$$= \frac{m_{TCA,tot}}{V_T\left[K_D \rho_b + \theta + K_H'(\varepsilon - \theta)\right]} = \frac{13'250\ \text{kg}}{5'655\ \text{m}^3\left[10^{-5}\frac{\text{m}^3}{\text{g}} \cdot \frac{1000\ \text{g}}{\text{kg}} \cdot 1'989.8\frac{\text{kg}}{\text{m}^3} + 0.1\frac{\text{m}^3}{\text{m}^3} + 0.56\ (0.15)\right]}$$

$$= 0.117\ \frac{\text{kg}}{\text{m}^3}$$

$$C_{TCA,s} = K_D C_{TCA,aq} = 10^{-5}\frac{\text{m}^3}{\text{g}} \cdot 1'000\frac{\text{g}}{\text{kg}} \cdot 0.117\frac{\text{kg}}{\text{m}^3} = 1.17 \cdot 10^{-3}\frac{\text{kg}}{\text{kg}}$$

$$C_{TCA,g} = K_H' C_{TCA,aq} = 0.56 \cdot 0.117\ \frac{\text{kg}}{\text{m}^3} = 0.070\ \frac{\text{kg}}{\text{m}^3}$$

Calculate the amount of time the removal of 95% of TCA will require.

$$\frac{dm_{TCA,tot}}{dt} = -C_{TCA,g} * Q = -K_H^{`} * C_{TCA,aq} * Q$$

$$\frac{dm_{TCA,tot}}{dt} = \frac{-K_H^{`} * m_{TCA,tot} * Q}{V_T * (K_D \rho_b + \theta + K_H^{`}(\varepsilon - \theta))}$$

$$\int_{m(t_0)}^{m(t)} \frac{dm_{TCA,tot}}{m_{TCA,tot}} = \int_{t_0}^{t} \frac{-K_H^{`} * Q * dt}{V_T * (K_D \rho_b + \theta + K_H^{`}(\varepsilon - \theta))}$$

$$\ln\left(\frac{m_{TCA,tot}(t)}{m_{TCA,tot}(t_0)}\right) = -\frac{K_H^{`} Q}{V_T * (K_D \rho_b + \theta + K_H^{`}(\varepsilon - \theta))} t$$

for 95% removal, $\left(\frac{m_{TCA,tot}(t)}{m_{TCA,tot}(t_0)}\right) = 0.05$

t= 140 days

Additional comment:
Saturation concentration of TCA in the gas phase is given by the ideal gas law PV=nRT, rearranged:
PV=nRT => n/V= P/RT and to get the concentration in units of mass per volume, we multiply by the molecular weight of TCA:
So we have: $C_{sat,\ TCA}$= M_WP/RT

$$C_{sat,TCA} = \frac{M_W \cdot P_V}{RT} = \frac{133\ \frac{g}{\cancel{mol}} \cdot 0.13\ \cancel{atm}}{0.08205\ \frac{L \cdot \cancel{atm}}{\cancel{mol} \cdot \cancel{K}} \cdot 293 \cancel{K}}$$

$$C_{sat,TCA} = 0.73\ \frac{kg}{m^3}$$

The mass transfer rate is fast since there is a substantial gradient: the difference between the air saturation of TCA and the actual concentration is large.

Problem 4:

Bioventing vs. Soil Vapor Extraction

Initial: $C_{TPH,s} = 500\, mg\, \frac{TPH}{kg\ soil}$

Target: $C_{TPH,s} = 50\, mg\, \frac{TPH}{kg\ soil}$

Part 1: Bioventing

1. Oxygen utilization rate

$Q = 60\ \frac{m^3}{d}$

$C_{O_2} = 21\ \%\ \frac{m^3 O_2}{m^3 air}$

$V = 120\ m^3$

$\varepsilon_a = 0.3 - 0.05 = 0.25$ *this is air porosity* (*meaning the porosity filled with air, so we must remove the porosity filled with water*)

$\rho_b = 1{,}400\ kg/m^3$

$\rho_{wb} = \frac{M_s + M_L}{V_T} = \rho_b + \rho_L \theta = 1{,}400 + 997 * 0.05 = 1{,}450\ kg/m^3$

$Q = \frac{k_o V \varepsilon_a}{C_{O_2}} \rightarrow \qquad k_o = \frac{Q C_{O_2}}{V \varepsilon_a}$

$\rightarrow \qquad k_o = \frac{60\ \frac{\cancel{m^3 air}}{day}\ 21\ \%\ \frac{m^3 O_2}{\cancel{m^3 air}}}{120\ \cancel{m^3 soil} * 0.25\ \frac{m^3 air}{\cancel{m^3 soil}}}$

$\rightarrow \qquad k_o = 42\ \%\ \frac{m^3 O_2}{m^3 air*day}$

2. Biodegradation rate

$D_{O_2} = 1{,}330\ \frac{gO_2}{m^3 O_2}$

$C = ratio\ of\ Carbon\ to\ O_2 = 0.3\ \frac{g\ of\ Carbon}{g\ of\ O_2}$

$k_B = \frac{\frac{k_o}{100} * \varepsilon_a * D_{O_2} * C}{\rho_{wb}}$

$\rightarrow k_B = \frac{\frac{\frac{42}{100} \cancel{m^3 O_2}}{\cancel{m^3 air}*day} * 0.25 \frac{\cancel{m^3 air}}{\cancel{m^3 soil}} * 0.3 \frac{g\ of\ C}{\cancel{g\ of\ O_2}} * 1{,}330 \frac{\cancel{gO_2}}{\cancel{m^3 O_2}}}{1{,}450 \frac{kgsoil}{\cancel{m^3 soil}}} = 0.03\ \frac{g\ of\ TPH\ C}{kg\ soil\ *day}$

3. First-order kinetics

$C_t = C_0 e^{-k_B t}$

$C_t = C_0 * e^{-3*10^{-5} \frac{kgTPH}{kgsoil*day} * t}$

$t = \frac{\ln\left(\frac{0.05}{0.5}\right)}{-k_B} = 210\ years$ (very long! We should use a higher flow rate)

Part 2: Soil Vapor Extraction

1. $C_{TPH,g} \; = ?$

$Q = 120 \dfrac{m^3}{day}$
$V_T = 6 * 20\, m^2 = 120\, m^3$
$V_G = (\varepsilon - \theta)V_T = 0.25 * 120\, m^3 = 30\, m^3$
$V_L = V_T\varepsilon - V_G = 120\, m^3 * 0.3 - 30\, m^3 = 6\, m^3$
$M_L = 6\, m^3 * 997 \dfrac{kg}{m^3} = 5{,}982\, kg$
$M_s = \rho_b V_T = 168{,}000\, kg\ dry\ soil$

$$C_{TPH,g} = \frac{K_H}{K_D} C_{TPH,s} = \frac{2.08}{0.03 \frac{m^3}{kg}} 500 \frac{mg}{kg} = 34.7 \frac{g}{m^3}$$

2. How long to reach the regulatory goal?

$\dfrac{dm_{TPH,tot(t)}}{dt} = -C_{TPH,g}(t) * Q$
$\rightarrow \int \frac{dm_{TPH,tot}}{dt}(t) * \; dt = -\int \frac{K_H m_{TPH,tot}(t)}{M_s K_D + K_H V_G + V_L} Q * dt$
$\rightarrow \int \frac{dm_{TPH,tot}}{m_{TPH,tot}} = -\int \frac{K_H Q}{M_s K_D + K_H V_G + V_L} * dt$
$\rightarrow \ln\left(\frac{m_{TPH,tot}(t)}{m_{TPH,tot}(t_0)}\right) = -\frac{K_H Q}{M_s K_D + K_H V_G + V_L}(t - \cancel{t_0})$
$\rightarrow \ln\left(\frac{\frac{C_{TPH,s,t}}{K_D}(M_s K_D + K_H V_G + V_L)}{\frac{C_{TPH,s,t_0}}{K_D}(M_s K_D + K_H V_G + V_L)}\right) = -\frac{K_H Q}{M_s K_D + K_H V_G + V_L} t$
$\rightarrow \ln\left(\frac{C_{TPH,s,t}}{C_{TPH,s,t_0}}\right) = -\frac{K_H Q}{M_s K_D + K_H V_G + V_L} t$

$\rightarrow \ln\left(\frac{50}{500}\right) = -\frac{K_H Q}{M_s K_D + K_H V_G + V_L} t$
$\rightarrow t = -\frac{\ln(0.1)}{0.0488} \sim 47\ days$

<u>What is the best solution?</u>
SVE is faster in this case, we should use about x100 higher flow rate to have reasonable bioventing result, which means higher energy cost.