**ENV 504**
**Remediation of soils and groundwater**

**Final exam 2024 – solution**

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## Problem 1: Bioremediation and air stripping

$C_{aq,TCE,0} = 1{,}000\ \mu g/L$

$C_{aq,toluene,0} = 10\,\frac{mg}{L}$

$Y = 0.007\,\frac{g_{cells}}{mg}$

$b = 10^{-4}\ d^{-1}$

$k = -0.05\,\frac{mg_{toluene}}{d.\,g_{cells}}$

$K_s = 0.1\ mg_{toluene}/L$

$B_0 = 1{,}000\,\frac{mg_{cells}}{L}$

2. Concentration of oxygen needed for complete oxidation of toluene to $CO_2$

$C_6H_5CH_3 + 9O_2 \rightarrow 7CO_2 + 4H_2O$

$$C_{aq,O_2} = 9 * \frac{C_{aq,toluene,i}}{M_{toluene}} * M_{O_2} = 9 * 10\,\frac{mg}{L} * \frac{\left(32\,\frac{g}{mol}\right)}{\left(7 * 12 + 8\,\frac{g}{mol}\right)} = 31.3\ mg/L$$

3. Concentration of toluene after 200 days ($O_2$ not limiting)

$$\frac{dC}{dt} = k\,\frac{B_0 + Y(C_0 - C)}{K_s + C}$$

$C_0 \gg K_s\ and\ B_0 \gg YC_0$ → zeroth order no growth: $C = C_0 + kB_0t$

After 200 days:

$$C_{aq,toluene,200} = 10\,\frac{mg}{L} - \frac{0.05mg_{toluene}}{d.\,gcells} * 1{,}000\,\frac{mg_{cells}}{L} * \frac{1\ g}{1000\ mg} * 200\ days$$
$$= 0\ mg/L$$

4. Total mass of TCE in 1m$^3$ of aquifer

$$m_{TCE,0} = C_{aq,TCE,0}(\epsilon + \rho_b K_D) = 1{,}000\,\frac{\mu g}{L}\left(0.3 + 1.75\,\frac{g}{mL} * 0.1\,\frac{mL}{g}\right)$$
$$= 475\ mg_{TCE}/m^3_{aquifer}$$

5. Concentration of TCE after 200 days in 1 m$^3$ of groundwater

Second-order batch reactor: $C_t = C_0/(1 + ktC_0)$

$$C_{aq,TCE,200} = \frac{1{,}000\,\frac{\mu g}{L}}{1 + 0.07\,\frac{L}{mg.d} * 200\ d * 1{,}000\,\frac{\mu g}{L} * \frac{1\ mg}{1{,}000\ \mu g}} = 67\ \mu g/L$$

6. TCE left after 200 days:

$$\frac{m_{TCE,200}}{m_{TCE,0}} = \frac{C_{aq,TCE,200}}{C_{aq,TCE,0}} = \frac{67}{1000} = 6.7\%$$

7. Effluent concentration of TCE from air stripping tower (20°C)

$$R = \frac{K_H Q_A}{Q_w} = 0.415 * 160 = 66.4$$

$$L = \frac{Q_w \rho_L}{S} = 60\,\frac{L}{s} *\ 0.997\,\frac{kg}{L} * \frac{1}{\pi 0.3^2\ m^2} = 212\,\frac{kg}{m^2 s}$$

$$L_M = \frac{L}{MW} = 212\,\frac{kg}{m^2 s} * \frac{1}{18\,\frac{g}{mol}} = 11{,}778\,\frac{mol}{m^2 s}$$

$$HTU = \frac{11{,}778\,\frac{mol}{m^2 s}}{55.6\,\frac{mol}{m^3} * 77\,\frac{m^2}{s}} = 2.75\ m$$

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

$$= 490 * 5.3 * 10^{-4} \left(\frac{212}{1.002 * 10^{-3}}\right)^{1-0.28} \left(\frac{1.002 * 10^{-3}}{997 * 5.3 * 10^{-4}}\right)^{0.5} = 77\,\frac{m^2}{s}$$

$$NTU = \frac{5.5}{2.75} = 2$$

Finally extracting the outlet concentration:

$$\ln\left(\frac{\left(\frac{C_{in}}{C_{out}}\right)(R-1) + 1}{R}\right) = \frac{NTU(R-1)}{R} = 1.97$$

$$\frac{C_{in}}{C_{out}} = \frac{Re^{1.97} - 1}{R - 1} = 7.27$$

$$C_{out} = 137.5\ \mu g/L$$

8. Compare the two approaches

Cometabolism: in-situ, lower concentration reach, but additional oxygen and toluene needed ($O_2$ concentration in question 2. is higher than saturation, and toluene concentration after 200 is 0 mg/l which is not possible, degradation will stop before)

Air-stripping: we can’t extract information on cost or duration because we don’t have the total volume to treat

**Problem 2: Adsorption**

$C_{PAC} = 2.7\ mg/L$

$\log(C_s) = 0.008 + 0.85 * \log(C_{aq})$

$C_{in} = 6\ \mu g/L$

1. Is absorption a feasible strategy?

Mass balance when equilibrium aqueous concentration reaches legal limit $C_t = 0.05\ \mu g/L$, with N the number of batches (1,000 needed prior to regeneration for the strategy to be economically feasible). We consider $C_{out} = 0\ \mu g/L$ for all batches, because 0.05 ug/L << 6 ug/L.

$N * V_{batch} * (C_{in} - C_{out}) = C_{PAC} V_{batch} C_s$

$N C_{in} = C_{PAC} C_s$

Sorbed concentration when Cout reaches 0.05 ug/L:

$$C_s = 10^{0.008+0.85*\log(0.05)} = 1.02 * 0.05^{0.85} = 0.08\frac{mg}{mg}$$

$$N = 2.7\frac{mg}{L} * \frac{0.08\frac{mg}{mg}}{6\frac{\mu g}{L} * \left(\frac{1\ mg}{1000\ \mu g}\right)} = 36$$

The carbon will be exhausted after 36 cycles so the strategy is not economically viable.

2. Concentration of PAC to use to achieve desired removal

$$C'_{PAC} = C_{PAC} * \frac{1{,}000}{N} = 75\frac{mg}{L}$$

**Problem 3: Biopiles**

1. Volume of water to add to each biopile

$V_L' = V_T\theta' = 500 * 0.8 * 0.2 = 80\ m^3$

$V_L = V_T\theta = 500 * 0.1 = 50\ m^3$

$V_{added} = V_L' - V_L = 30\ m^3/biopile$

2. Mass of ammonium sulfate and trisodium phosphate to be added to each biopile

Number of biopiles:

$$N = \frac{10{,}000\ m^3}{500\ m^3} = 20$$

Moles of C from benzene per biopile:

$$n_{benzene} = \frac{m_{benzene}}{M_{benzene}} = \frac{\frac{2{,}000}{20} kg}{78 * 10^{-3} \frac{kg}{mol}} = 1{,}282\ mol$$

$n_C = 6 * n_{benzene} = 7{,}692\ mol$

$n_N = 641\ mol; m_N = 641\ mol * \frac{132}{2}\frac{g}{mol} = 42\ kg$

$n_P = 64\ mol; m_P = 64\ mol * 380\frac{g}{mol} = 24\ kg$

3. Amount of $O_2$ present in each biopile sufficient for the degradation of benzene?

$$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$$

Quantity of $O_2$ needed per biopile:

$$n_{O_2,needed} = 7.5 * 1{,}282\ mol = 9{,}615\ mol$$

Quantity of $O_2$ available (gas phase and dissolved):

$$V_G = V_T - V_S - V_L' = V_T - \frac{M_S}{\rho_s} - V_L'$$

$$M_s = \rho_{wb} * V_T - \theta V_T = 500\ m^3 \left(1{,}875\frac{kg}{m^3} - 997\frac{kg}{m^3} * 0.1\right) = 887.5 * 10^3 kg$$

$$V_G = 500\ m^3 - \frac{887.5 * 10^3 kg}{2{,}500\frac{kg}{m^3}} - 80m^3 = 65\ m^3$$

$V_{O_2} = 21\% * V_G = 13{,}650\ L$

$$n_{O_2,g} = \frac{13{,}650}{22.4\ L/mol} = 610\ mol$$

$$n_{O_2,aq} = V_L' C_{O_2,sat} = 80{,}000\ L * 9.2\frac{mg}{L} * \frac{1}{32\frac{g}{mol}} = 23\ mol$$

$$n_{O_2,tot,available} = 633\ mol \ll n_{O_2,needed}$$

4. Number of air volumes needed:

$$N = \frac{n_{O_2,needed} - n_{O_2,available}}{n_{O_2,g}} = \frac{9{,}615 - 633}{610} = 15$$

5. How long to treat the entire amount of soil assuming sufficient oxygen and nutrient applied?

$$k = 1\frac{mg}{kg_{dry\ soil}d}$$

$$C_t = 30\ mg/kg_{dry\ soil}$$

$$C_0 = C_{aq}K_D = \frac{\frac{m_{benzene}}{N}}{K_D M_S + K_H V_G + V_L'} K_D$$
$$= \frac{\frac{2{,}000}{20}kg}{(0.03 * 887.5 * 10^3 + 2.08 * 65 + 80)m^3} * 0.03\frac{m^3}{kg} = 111\frac{mg}{kg}$$

Treatment duration:

$$t = \frac{C_0 - C_t}{k} = \frac{111\frac{mg}{kg} - 30\frac{mg}{kg}}{\frac{1mg}{kg.d}} = 80\ days$$