Solution Exam 2025

For simplicity of typing, all subscripts are preceded by an underscore rather than actually being a subscript.

PROBLEM 1

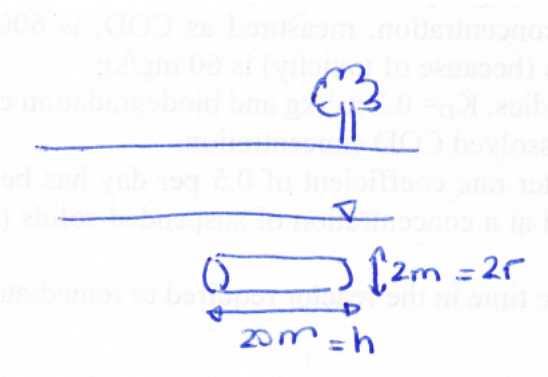
Use the same unit throughout (kg and m^3)

1,4-dioxane ($C_4H_8O_2$) C_aq,i = 1000 µg/L = 10^{-3} kg/m^3; C_aq,f = 10 µg/L = 10^{-5} kg/m^3

ρ_b = 1750 kg/m^3

ε = 0.4

K_D = 10^{-6} m^3/kg



Part 1: Partitioning

V_T = $\pi r^2 h = \pi(1\ m)^2(20\ m) = 62.8\ m^3$

V_L = V_T ε = 62.8 m^3(0.4) = 25.12 m^3

M_s = V_Tρ_b = 62.8 m^3 × 1750 kg/m^3 = 109,900 kg

A. Total dioxane mass (no gas phase because this is an aquifer)

m_total,diox = m_aq,diox + m_s,diox= C_aq*(V_L + K_D*M_S)

m_total,diox = 10^{-3} kg/m^3 *[25.12 m^3 + 10^{-6} m^3/kg × 109,900 kg]= 2.52 × 10^{-2} kg

B. Mass on solid

m_solid,diox = C_aq *M_s *K_D= 10^{-3} kg/m^3 × 109,900 kg × 10^{-6} m^3/kg= 1.1 × 10^{-4} kg (= 0.11 g)

C_s,diox = C_aq *K_D= 10^{-3} kg/m^3 × 10^{-6} m^3/kg= 10^{-9} kg diox/kg solid

C. Mass in groundwater

m_aq,diox = C_aq* V_L= 10^{-3} kg/m^3 × 25.12 m^3= 2.51 × 10^{-2} kg

So, the large majority of the mass of contaminant is in the aqueous phase (99.6%). We can ignore the solid phase-associated contaminant.

2. Part 2: In situ biodegradation

A. CB1190

$$C_4H_8O_2 + 6H_2O \rightarrow 4CO_2 + 20H^+ + 20e^-$$

$$\underline{(O_2 + 4H^+ + 4e^- \rightarrow 2H_2O) \times 5}$$

$$C_4H_8O_2 + 5O_2 \rightarrow 4H_2O + 4CO_2$$

Ratio: 5:1 for O_2:dioxane (molar). How many moles of dioxane are present? (MW=88 g/mol)

n_dioxane = $(2.52 \times 10^{-2}$ kg / 88 g/mol) × 1000 g/kg = 0.29 moles

n_O_2 = 5 × (0.29) = 1.45 moles needed

m_O_2 = 1.45 mol × 32 g/mol = 46.4 g O_2

C_O_2,needed = 46.4 g / 25.12 m^3 × 1 m^3/1000 L × 1000 mg/g= 1.85 mg/L

1.85 mg/L < solubility of O_2 in water. Therefore, there is sufficient dissolved O_2 if aquifer is fully oxygenated.

B. G4

$$C_7H_8 + 14H_2O \rightarrow 7CO_2 + 36H^+ + 36e^-$$

$$\underline{(O_2 + 4H^+ + 4e^- \rightarrow 2H_2O) \times 9}$$

$$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O$$

Ratio: 9:1 for O_2:toluene (molar).

Need 5 moles of toluene per mole of dioxane→ 45 mol O_2/mol dioxane

n_O_2 = 0.29 mol dioxane × 45 = 13.05 mol O_2 needed for toluene oxidation

but we still need the O_2 for the oxidation of dioxane itself. n_O_2 = 5 × (0.29) = 1.45 moles needed (from above)

m_O_2 = (13.05 + 1.45) mol × 32 g/mol = 464 g O_2

C — Calculate C_min for CB1190 (direct dioxane degradation)

C_min = bK_s / (Yk − b) => Minimum concentration of substrate (dioxane) needed for biomass growth.If the concentration falls below this value, no growth will occur.

b = death rate = 0.001 d^{-1}

K_S = half-velocity constant = 1 mg/L

Y = growth yield coefficient = 0.09 mg protein/mg dioxane

k = degradation rate constant (normalized to biomass) = 1.1 mg dioxane/(mg protein·d)

X = biomass concentration = 100 mg protein/L groundwater

C_min =[0.001 d^{-1} × 1 mg/L] /[0.09 (mg protein/mg dioxane) × 1.1 (mg dioxane/(mg protein·d)) − 0.001 d^{-1}]

C_min = 0.0102 mg/L = 10.2 µg/L => C_min < C_aq,i, but very close to C_aq,final. But this is still in the feasible range.

Half-life of dioxane = ?

We need k' the first-order rate constant based on k and K_S and X (from above).

k' = (k/K_S)X

k' = [1.1 mg dioxane/(mg protein·d) × 100 mg protein/L]/ 1 mg dioxane/L= 110 d^{-1}

t_1/2 = ln 2 / k'= 0.693 / 110 d^{-1}= 0.0063 d= 0.15 h

D. Half-life of toluene

k' = (k/K_s)X

X = 1,000 mg/L

k = 0.08 mg toluene/(mg protein·h)

K_S = 22 mg/L

k' =[0.08 mg toluene/(mg protein·h) / 22 mg toluene/L]× 1000 mg protein/L= 3.63 h^{-1}

t_1/2 = 0.693 / 3.63 h^{-1}= 0.19 h

Very similar half-life for toluene and dioxane (with direct oxidation)

E. best metabolism?

As dioxane is oxidized 5× more slowly than toluene in cometabolism:

t_1/2,dioxane,comet = (5 × 0.19 h)= 0.95 h

Therefore, it is clear that direct oxidation is faster.

Part 3: Pump and treat with GAC adsorption

Q = 20 L/min = 0.02 m^3/min

C_i,s (mg/g) = 1.18 × 10^4 [C_i,aq (mg/cm^3)]^(1/1.01)

V_bed = 0.05 m^3

ρ_b = 500 kg/m^3

A — breakthrough time?

$C_{i,aq} = 10^{-3}$ kg/m³ × 1000 g/kg= 1 g/m³= 10^{-3} mg/cm³

$C_{i,s} = 1.18 \times 10^{-4} \times (10^{-3})^{(1/1.01)}$= 12.6 mg/g= 12.6 g/kg

$t_b = [C_{i,s} \times \rho_b \times V_{bed} \times (0.75)] / [Q \times C_{i,aq}]$

= [12.6 g_diox/kg_GAC × 500 kg/m³ × 0.05 m³_GAC × 0.75] / [0.02 m³/min × 1 g_diox/m³]

= 236.25 / 0.02 min

= 11,812.5 min

= 8.2 days

This is very short for a GAC system

B — Mass of contaminant / GAC needed

$m_{total,diox} = 2.52 \times 10^{-2}$ kg dioxane

Load on GAC $C_{i,s} = 1.26 \times 10^{-2}$ kg dioxane/kg GAC

Mass GAC needed $M_{GAC} = m_{total,diox} / C_{i,s}$= (2.52 × 10^{-2} kg diox) / (1.26 × 10^{-2} kg diox/kg GAC)= 2 kg GAC

How much GAC in bed: $M_{GAC} = V_{bed} \rho_{GAC}$= 0.05 m³ × 500 kg/m³= 25 kg

We would be using <10% of the bed, so should use a smaller bed.

If V = 0.01 m³: $t_{b,small} = t_b \times (0.2)$= 1.64 d

Need only 5 kg of GAC, which is sufficient.

C. How long run the system?

For the original bed size, breakthrough occurs in 8.2 days.

As the flow rate is 0.02 m³/min, it represents:28.8 m³/day

Since there is only V_L = 25.12 m³ and the great majority of dioxane is in the aqueous phase, we only need to run the system for 1 day.

The smaller size would work fine as well as the breakthrough is in 1.64 days, so after all the volume that needs to be treated has been treated.

Part 4: Overall comparison

Method	Pros	Cons
Direct biological oxidation	fast; no amendment	C_{min} close to $C_{aq,final}$, so may not reach target
Cometabolic biodegradation	degrade to low conc.	amend toluene to the aquifer (cost but risk in handling)
Pump-and-treat with GAC	Pros: well established; need little GAC	Cons: ex-situ; treat AC afterwards

Problem 2

V_T = 10 m^3

C_s,in = 600 mg/kg → C_s,out = 60 mg/kg

K_D = 0.2 m^3/kg

k = 0.5 d^{-1}

C_SS = 10 kg dry soil/m^3 slurry

ρ_s = M_s/V_s = 2600 kg/m^3

M_s= C_SS x V_T = 10 kg dry soil/m^3 slurry x 10 m^3= 100 kg

We can calculate the volume of solid in the slurry:

V_s = M_s/ρ_s = 100 kg / 2600 kg/m^3 = 0.038 m^3 ≪ V_T → neglect

We can neglect V_s so that V_T ~ V_L

Initial mass of contaminant:

m_i,total = C_i,in x C_SS x V_T = 600 mg/kg × 10 kg soil/m^3 × 10 m^3= 60 g

For a batch slurry reactor:

$$t = -\left[K_S ln\left(\frac{C_{i,aq}}{C_{i,aq,0}}\right) + K_D\left(C_{i,aq} - C_{i,aq,0}\right)\right]\left[\frac{Y(V_L + M_S K_D)}{X_w M_S K_b \mu_{s,max} K_D}\right]$$

C_aq,in = ?

When the soil is mixed with water, some of the contaminant will be transferred to the aqueous phase. So the C_s,in concentration **in original soil** will not be equal to C_s,in in **soil suspended in water**.

m_i,total = m_i,s + m_i,aq

= M_s x C_i,s + V_L x C_i,aq

= M_s x K_D x C_i,aq + V_L x C_i,aq

$$C_{i,aq} = \frac{m_{i,tot}}{V_L + K_D * M_S} = \frac{60\ \text{g}}{10\ \text{m}^3 + 0.2\frac{\text{m}^3}{\text{kg}} * 100\ \text{kg}} = 2\frac{g}{m^3}$$

The final aqueous concentration is in equilibrium with the final solid-associated contaminant concentration:

C_i,aq,final = C_i,s,final / K_D= [60 mg/kg] / [0.2 m³/kg]= 300 mg/m³= 0.3 g/m³

$$t = -\begin{bmatrix} 2.12\frac{mg}{g} * \\ ln\left(\frac{0.3}{2}\right) + 0.2\frac{m^3}{kg} * \\ (0.3 - 2) \end{bmatrix} * \left[\frac{0.34\frac{mg}{mg}\left(10\ m^3 + 100\ kg * 0.2\frac{m^3}{kg}\right)}{2\frac{mg}{L} * 100\ kg * 0.167\frac{L}{g} * 0.29\ h^{-1} * 0.2\frac{m^3}{kg}}\right]$$

t= 2.3 h

Problem 3

P_r= pressure at radial distance r =8 *10^5 g/(cm.s^2)
P_w= pressure at extraction well= 3 *10^5 g/(cm.s^2)
P_{RI}= pressure at radius of influence = 1 atm
r= radial distance from extraction well= 2.5 m
R_I= radius of influence where pressure=atm. pressure= **?**
R_w= well radius of extraction well= 0.1m

Volume of contaminated zone: V= 10 m^2 x 2m= 20 m^3

Convert pressures to atm
P_r= pressure at radial distance r =8 *10^5 g/(cm.s^2) x 1 atm/1.013 *10^6 g/(cm.s^2)=0.789 atm
P_w= pressure at extraction well= 3 *10^5 g/(cm.s^2)= 0.296 atm
P_{RI}= pressure at radius of influence = 1.013 *10^6 g/(cm.s^2)= 1 atm

$P_r^2 - P_w^2 = (P_{RI}^2 - P_w^2)\frac{ln\left(\frac{r}{R_w}\right)}{ln\left(\frac{R_I}{R_w}\right)}$ with pressures in atm

$$\frac{P_r^2 - P_w^2}{(P_{RI}^2 - P_w^2)} = \frac{ln\left(\frac{r}{R_w}\right)}{ln\left(\frac{R_I}{R_w}\right)}$$

$$\frac{(P_{RI}^2 - P_w^2) * ln\left(\frac{r}{R_w}\right)}{P_r^2 - P_w^2} = ln\left(\frac{R_I}{R_w}\right)$$

$$\frac{\left(1 - 0.296^2\right) * ln\left(\frac{2.5}{0.1}\right)}{0.789^2 - 0.296^2} = ln\left(\frac{R_I}{0.1}\right)$$

R_I=24.2 m

Height of screen=8m
Soil porosity=0.4
Soil volumetric moisture content (θ)= 0.2
Soil wet bulk density ρ_{wb} =1.40 g/cm^3
Soil dry bulk density ρ_b= 1.20 g/cm^3
Permeability of the formation k= 10^{-10} m^2
Viscosity of air μ= 1.8*10^{-4} g/cm.s
Ambient pressure=1.013 *10^6 g/(cm.s^2)= 1 atm
P_r= pressure at radial distance r =8 *10^5 g/(cm.s^2)
P_w= pressure at extraction well= 3 *10^5 g/(cm.s^2)

Calculate the water pumping rate

$$Q_w = H\left(\frac{\pi k}{\mu}\right)\left(\frac{P_w}{ln\left(\frac{R_w}{R_I}\right)}\right)\left(1 - \left(\frac{P_{RI}}{P_w}\right)^2\right)$$

$$Q_w = 8m * \left(\frac{3.14 * 10^{-10} m^2}{1.8 * 10^{-4} \frac{g}{cm.s}}\right)\left(\frac{3 * 10^5 \frac{g}{cm.s^2}}{ln\left(\frac{0.1}{24.2}\right)}\right)\left(1 - \left(\frac{1.013 * 10^6 \frac{g}{cm.s^2}}{3 * 10^5 \frac{g}{cm.s^2}}\right)^2\right)$$

Qw= 7.95 m^3/s

Number of wells needed

$$N = \frac{1.2 * A}{\pi * R_I^2} = \frac{1.2 * 10\ m^2}{\pi * 24.2^2\ m^2} = 0.006 \ll 1\ \boldsymbol{only\ one\ well\ needed}$$