

Lecture Notes week 8

Slide 21 – Land treatment case study

Land treatment of petroleum refinery waste

Time of application (days after initial application)	Amount of applied waste (tons)	Oil concentration in applied waste (%)
0	20.1	16.5
110	30.6	13.1
229	30.6	16.8
298	24.7	18.5

- 1) Calculate oil soil loading
Corresponds to tons of oil applied
Oil applied= waste (tons) * % oil concentration/100

Days	Applied oil (t)
0	3.3
110	4.0
229	5.1
298	4.6

- 2) Calculate the amount of oil that is added to ZOI at each application:

$$m_{oil,i} = C_{oil,waste,i} * M_{waste}$$

$$C_{oil,ZOI} = \frac{m_{oil,i}}{M_{ZOI}}$$

We need to calculate the mass of ZOI:

$$M_{ZOI} = V_{ZOI} * \rho_{soil} = 15m * 36m * 0.1m * 1,538 \frac{kg}{m^3} = 83 tons$$

The mass of ZOI does not change with soil addition, because it is defined as the first 10 cm below the surface of the land treatment facility.

Incremental increase ZOI concentration (%)= (mass of oil applied)/ M_{ZOI} *100

Days	Applied oil (t)	Incremental increase ZOI concentration (%)
0	3.3	4.0
110	4.0	4.8
229	5.1	6.2
298	4.6	5.5

- 3) What is the oil biodegradation rate?

The oil added is degraded by microbial consumption, after 368 days it is said that the average concentration of oil remaining is 13%.

NB: if the oil had not been degraded we would have: 4.0% + 4.8% + 6.2% + 5.5% = 20.5%!

We assume first-order kinetics for oil biodegradation (this is often justified for soils):

$$C_t = C_0 e^{-k(t-t_0)}$$

We can apply this equation for each batch (i) of oil addition:

$$C_{t,i} = C_{0,i} e^{-k(t-t_{0,i})}$$

With $C_{0,i}$ and $C_{t,i}$ the initial and final concentration (only considering the added batch) of oil in the ZOI, and $t_{0,i}$ the number of days after start at which the batch was applied to the land treatment facility.

So, the remaining oil after 368 days (13%) is:

$$\begin{aligned} 13\% &= C_{368,1} + C_{368,2} + C_{368,3} + C_{368,4} \\ &= 4.0\% e^{-k*(368-0)} + 4.8\% e^{-k*(368-110)} + 6.2\% e^{-k*(368-229)} + 5.5\% e^{-k*(368-298)} \\ &= 4.0\% e^{-k*368} + 4.8\% e^{-k*258} + 6.2\% e^{-k*139} + 5.5\% e^{-k*70} \end{aligned}$$

From that we can calculate k (trial and error):

$$k = 0.0025 \text{ days}^{-1}$$

And the half-life:

$$t_{\frac{1}{2}} = -\frac{\ln(0.5)}{k} = 277 \text{ days}$$

Slide 49 – Batch operation

$$C_{i,s,0} = 200 \frac{mg}{kg} \text{ and } C_{i,s,f} = 10 \frac{mg}{kg}$$

$$k = 0.5 \text{ h}^{-1}$$

$$V_L = 0.1 \text{ m}^3$$

$$M_S = 5 \text{ kg}$$

$$K_D = 2 \frac{m^3}{kg}$$

For a batch reactor, with first order kinetics: $C_t = C_0 e^{-kt}$, with C being the aqueous concentration because microorganisms use dissolved compounds.

We know the concentration in soil, so before mixing with water to obtain the sludge → we must first calculate what is the initial concentration in water after partitioning, no gas phase in the reactor:

$$\begin{aligned} m_{i,total,in} &= m_{i,s,in} + m_{i,aq,in} = C_{i,s,in} * M_S + C_{i,aq,in} * V_L \\ &= C_{i,aq,in} * K_D * M_S + C_{i,aq,in} * V_L = C_{i,aq,in} * (M_S K_D + V_L) \end{aligned}$$

$$\begin{aligned} m_{i,total,in} &= m_{i,s,0} + m_{i,aq,0} = C_{i,s,0} * M_S + C_{i,aq,0} * V_L \\ &= C_{i,aq,0} * K_D * M_S + C_{i,aq,0} * V_L = C_{i,aq,0} * (M_S K_D + V_L) \end{aligned}$$

$$C_{i,aq,0} = \frac{m_{i,total}}{M_S K_D + V_L} = \frac{200 \frac{mg}{kg} * 5 \text{ kg}}{5 \text{ kg} * 2 \frac{m^3}{kg} + 0.1 \text{ m}^3} = 99 \frac{mg}{m^3}$$

The final concentration in water, is calculated from equilibrium with final concentration in the solid phase where contaminant concentration in the solid reaches desired concentration:

$$C_{i,aq,f} = \frac{C_{i,s,f}}{K_D} = \frac{10 \frac{mg}{kg}}{2 \frac{m^3}{kg}} = 5 \frac{mg}{m^3}$$

We can now calculate t :

$$t = -\frac{\ln\left(\frac{C_{i,aq,f}}{C_{i,aq,0}}\right)}{k} = 6 \text{ h}$$

Slide 51 - CSTR

For a CSTR:

- $C_0 = C_{in}$ and $C_t = C_{out}$
- first order kinetics: $\frac{C_{out}}{C_{in}} = \frac{1}{1+kt}$, with C the aqueous concentration

Same as what was done for the previous example:

Same as before, we know the concentration in soil, so before mixing with water to obtain the sludge
→ we must first calculate what is the initial concentration in water after partitioning, no gas phase in the reactor:

$$C_{i,aq,in} = \frac{m_{i,total,in}}{M_S K_D + V_L} = \frac{200 \frac{mg}{kg} * 5 kg}{5 kg * 2 \frac{m^3}{kg} + 0.1 m^3} = 99 \frac{mg}{m^3}$$

The final concentration in water, is calculated from equilibrium with final concentration in the solid phase where contaminant concentration in the solid reaches desired concentration:

$$C_{i,aq,out} = \frac{C_{i,s,out}}{K_D} = \frac{10 \frac{mg}{kg}}{2 \frac{m^3}{kg}} = 5 \frac{mg}{m^3}$$

$$t = \frac{1}{k} \left(\frac{C_{in}}{C_{out}} - 1 \right) = 37.6 h$$