

1. Treatment by GAC

Ⓐ Estimate/calculate conc. of adsorbed DCE.

Given $UR_{min} = 54 \frac{g \text{ GAC}}{m^3 \text{ water}}$... know $UR_{min} = \frac{C_I}{q_{eq}}$

$$\therefore q_{eq} = \frac{C_I}{UR} = \frac{700 \mu\text{g DCE} / \text{L water}}{54 \text{ g GAC} / \text{m}^3 \text{ water}} \cdot \frac{1000 \text{ L water}}{1 \text{ m}^3 \text{ water}}$$

$$q_{eq} = 12,963 \frac{\mu\text{g}}{\text{g}} \dots \text{let's say } \boxed{q_{eq} = 13,000 \mu\text{g/g}}$$

Ⓑ Estimate/calculate Freundlich K_F for DCE

$$12,963 \frac{\mu\text{g}}{\text{g}} = K_F (700 \frac{\mu\text{g}}{\text{L}})^{0.689}$$

$$\boxed{K_F = 142 \frac{\mu\text{g/g}}{(\mu\text{g/L})^{0.689}}}$$

Ⓒ Estimate/calculate Freundlich parameters for DCA

$$\frac{1}{n} = \frac{\beta RT / p_s}{\text{mol. wt.}} \dots \text{we don't know } \beta \dots \text{we could solve for } \beta \text{ by using the DCE data, but there is a short-cut}$$

$$\left(\frac{1}{n}\right)_{DCA} = \left(\frac{1}{n}\right)_{DCE} \cdot \left(\frac{p_s}{\text{mol. wt.}}\right)_{DCA} \div \left(\frac{p_s}{\text{mol. wt.}}\right)_{DCE}$$

$$\left(\frac{1}{n}\right)_{DCA} = (0.689) \cdot \frac{1.18 \text{ g/mol}}{98.96 \text{ g/mol}} \div \frac{1.22 \text{ g/mol}}{96.94 \text{ g/mol}}$$

$$\boxed{\frac{1}{n} = 0.653 \text{ for DCA}}$$

$$K_F = \frac{p_L \cdot W_0}{(C^{SL})^{1/n}} \dots \text{again, we don't know } W_0 \dots \text{we could solve for } W_0, \text{ but we don't have to... there is a short-cut}$$

$$(K_F)_{DCA} = (K_F)_{DCE} \cdot \left[\frac{p_L}{(C^{SL})^{1/n}}\right]_{DCA} \div \left[\frac{p_L}{(C^{SL})^{1/n}}\right]_{DCE}$$

$$(K_F)_{DCA} = 142 \frac{\mu\text{g/g}}{(\mu\text{g/L})^{0.689}} \cdot \frac{1.18 \text{ g/mol}}{(5.1 \times 10^6 \mu\text{g/L})^{0.653}} \div \frac{1.22 \text{ g/mol}}{(2.5 \times 10^6 \frac{\mu\text{g}}{\text{L}})^{0.689}}$$

$$\boxed{K_F = 147 \frac{\mu\text{g/g}}{(\mu\text{g/L})^{0.653}} \text{ for DCA}}$$

1. Continued

(d) Estimate UR_{min} for DCA

$$UR_{min} = \frac{C_I}{q_{e2}} \quad q_{e2} = \left[147 \frac{\mu\text{s}/\text{s}}{(\mu\text{s}/\text{L})^{0.653}} \right] \cdot (700 \frac{\mu\text{s}}{\text{L}})^{0.653}$$

$$q_{e2} = 10,600 \frac{\mu\text{s}}{\text{g}} \Rightarrow UR_{min} = \frac{700 \mu\text{s}/\text{L}}{10,600 \mu\text{s}/\text{g}} \cdot \frac{1000 \text{ L}}{1 \text{ m}^3}$$

$$UR_{min} = 66 \frac{\text{g GAC}}{\text{m}^3 \text{ water}}$$

... about 20% higher than previously estimated... so that is worse (more expensive)

(e) Estimate bed volumes treated, assuming thin MTZ

Use Θ_m if MTZ is infinitesimally thin

$$\Theta_m = \frac{\rho_f}{UR_{min}} \quad \text{or} \quad \Theta_m = \frac{\rho_f q_e}{C_I} \quad \dots \text{ same either way}$$

$$\Theta_m = \frac{(540 \text{ kg}/\text{m}^3)(1000 \text{ g}/\text{kg})}{66 \text{ g}/\text{m}^3} = 8200 \text{ bed volumes treated}$$

(f) Is GAC a good method?

This looks pretty good. If we can treat 8200 bed volumes before changing the GAC, that should be pretty economical. A usage rate of 66 g/m³ is not too bad. I think it will work.

(g) What if we hadn't caught the error?

The client would be expecting a usage rate of 54 g/m³, but instead the usage rate would actually be 66 g/m³. The operating costs will be 20% higher than expected. The client will not be happy!

2. Treatment by Air Stripping

(a) Air flow rate

$$S = \frac{H Q_a}{Q} \Rightarrow Q_a = S \cdot \frac{Q}{H} = (6.0)(0.0063 \text{ m}^3/\text{s}) / (0.92)$$

$$Q_a = 0.041 \text{ m}^3/\text{s}$$

(b) Estimate/calculate the Number of Transfer units (NTU)

$$\text{Given } S=6.0, \quad C_o = 700 \text{ mg/L}, \quad C_E = 7 \text{ mg/L}$$

$$\text{NTU} = \frac{S}{S-1} \ln \left\{ \frac{1 + \left(\frac{C_o}{C_E}\right)(S-1)}{3} \right\} = \frac{6}{5} \ln \left\{ \frac{1 + (100)(5)}{6} \right\}$$

$$\text{NTU} = 5.3$$

(c) Estimate/calculate the height of a transfer unit, HTU

$$\text{HTU} \times \text{NTU} = L \Rightarrow \text{HTU} = \frac{L}{\text{NTU}} = \frac{5.0 \text{ m}}{5.3}$$

$$\text{HTU} = 0.94 \text{ m}$$

(d) Estimate/calculate the cross-sectional area of the tower

$$\text{HTU} = \frac{Q/A}{K_L a} \Rightarrow A = \frac{Q/\text{HTU}}{K_L a} \quad \dots \text{ need } K_L a$$

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{k_L H} = \frac{1}{2.5 \times 10^{-4} \text{ m/s}} + \frac{1}{(0.92)(2.3 \times 10^{-3} \text{ m/s})} = 4473 \frac{\text{s}}{\text{m}}$$

$$K_L = 2.24 \times 10^{-4} \text{ m/s}, \quad a = 59.9 \text{ m}^2/\text{m}^3 \Rightarrow K_L a = 0.0134 \text{ s}^{-1}$$

$$A = \frac{(0.0063 \text{ m}^3/\text{s}) / (0.94 \text{ m})}{0.0134 \text{ s}^{-1}} = 0.50 \text{ m}^2$$

(e) Estimate H for DCA

$$H = \frac{P^{s+1}/RT}{C^{sL}} = \frac{(22,300 \text{ Pa}) / (8.314 \text{ Pa} \cdot \text{m}^3/\text{mol} \cdot \text{K})(291.15 \text{ K})}{(5.1 \text{ g/L})(1 \text{ mole}/98.96 \text{ g})(1000 \text{ L}/\text{m}^3)}$$

$$H = 0.1787 = 0.18$$

2. continued

(f) Why is it OK to use the same k_L k_G a_w for DCE, DCA?

The wetted area, a_w , does not depend on the chemical, only on the packing, flow rates, and dimensions of the tower. So clearly a_w does not change with chemical.

k_L depends on the aqueous diffusivity of the chemical.

k_G depends on the air-phase diffusivity of the chemical.

But these are likely to be very similar for DCE and DCA. The molecular weights and chemical structures of the two chemicals are very similar.

Very similar structures \Rightarrow very similar diffusion coefficients \Rightarrow very similar mass-transfer coefficients.

So we'll use the same k_L k_G a_w !

(g) Re-calculate S and HTU for DCA

$S = 1.174$

$$S = \frac{H Q_a}{Q} = \left(\frac{0.18}{0.92} \right) (6.0) \text{ using ratio of } H \Rightarrow \boxed{S = 1.2}$$

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{k_G H} = \frac{1}{2.5 \times 10^{-4} \text{ m/s}} + \frac{1}{(0.18)(2.3 \times 10^{-3} \text{ m/s})} = 6415 \frac{\text{s}}{\text{m}}$$

$$K_L = 1.56 \times 10^{-4} \frac{\text{m}}{\text{s}}, \quad a_w = 59.9 \frac{\text{m}^2}{\text{m}^3} \Rightarrow K_L a = 9.3 \times 10^{-3} \frac{\text{m}}{\text{s}}$$

$$\text{HTU} = \frac{Q/A}{K_L a} = \frac{(0.0063 \text{ m}^2/\text{s}) / (0.50 \text{ m}^2)}{9.34 \times 10^{-3} \text{ m/s}} = \boxed{1.35 \text{ m} = \text{HTU}}$$

(h) What effluent concentration could we achieve?

$$\text{NTU} = \frac{L}{\text{HTU}} = \frac{5.0 \text{ m}}{1.35 \text{ m}} = 3.7$$

$$\text{NTU} = \frac{S}{S-1} \ln \left\{ \frac{1 + \left(\frac{C_o}{C_e} \right) (S-1)}{S} \right\} \Rightarrow \exp \left[\frac{(S-1) \text{NTU}}{S} \right] = \frac{1 + \frac{C_o}{C_e} (S-1)}{S}$$

$$\frac{C_o}{C_e} = \left\{ S \exp \left[\frac{(S-1) \text{NTU}}{S} \right] - 1 \right\} / (S-1)$$

$$\frac{C_o}{C_e} = \left\{ (1.174) \exp \left[\frac{(0.174)(3.705)}{(1.174)} \right] - 1 \right\} / 0.174 = 5.94$$

$$C_e = \frac{C_o}{5.94} = \frac{700 \mu\text{g/L}}{5.94} \Rightarrow \boxed{C_e = 120 \mu\text{g/L}} \text{ not even close to meeting requirement!!}$$

2. continued

(c) If we hadn't caught the error...

Wow, that would have been a very unhappy client! If we had built this system according to $A=0.50\text{m}^2$ $Q_a=0.041\text{m}^3/\text{s}$ $L=5.0\text{m}$, expecting to reach $7\text{ }\mu\text{g/L}$ in the effluent, we actually would have been left with $120\text{ }\mu\text{g/L}$ in the effluent. The client might face big fines. Even turning up the air rate might not be sufficient (I am not sure, I didn't check).

Why so different? Now we see how important Henry's constant is for air stripping! It is the only thing that changed from DCE to DCA. The lower value of H affects both S and $K_L a$. Henry's constant is really the key parameter for determining the success of air stripping.

3. Treatment by Advanced Oxidation (O_3/H_2O_2)

(a) Estimate/calculate concentration of DCE.

We have $[DCE] = \frac{C_I}{1+k_1\tau}$ where $k_1^{app} = k_R [\cdot OH]$

The problem is we don't know $[\cdot OH]$.

$$[DCE] = \frac{7.2 \times 10^{-6} \text{ M}}{1 + (6.8 \times 10^9 \text{ L/mol}\cdot\text{s})(1586 \text{ s}) [\cdot OH]} = \frac{7.2 \times 10^{-6} \text{ M}}{1 + (1.078 \times 10^{13} \text{ L/mol}) [\cdot OH]}$$

Also

$$[\cdot OH] = \frac{(7.0 \times 10^{-4} \text{ s}^{-1})(0.04 \text{ atm}) / (70 \text{ atm}\cdot\text{L/mol})}{(2.7 \times 10^7 \text{ L/mol}\cdot\text{s})(2.1 \times 10^{-4} \text{ M}) + (8.5 \times 10^6 \text{ L/mol}\cdot\text{s})(1.6 \times 10^{-3} \text{ M}) + (3.9 \times 10^8 \text{ L/mol}\cdot\text{s})(9.0 \times 10^{-6} \text{ M}) + (6.8 \times 10^9 \text{ L/mol}\cdot\text{s})[DCE]}$$

$$[\cdot OH] = \frac{4.0 \times 10^{-7} \text{ mol/L}}{22780 \text{ s}^{-1} + (6.8 \times 10^9 \text{ L/mol}\cdot\text{s})[DCE]}$$

Two equations, two unknowns.

These look ugly to solve simultaneously.

Different ways to solve these simultaneously... I will do it iteratively.

Guess $[DCE] = 7.2 \times 10^{-8} \text{ M} \Rightarrow [\cdot OH] = 1.72 \times 10^{-11} \frac{\text{mol}}{\text{L}}$

$\Rightarrow [DCE] = 3.86 \times 10^{-8} \text{ M} \Rightarrow [\cdot OH] = 1.74 \times 10^{-11} \frac{\text{mol}}{\text{L}}$

$\Rightarrow [DCE] = 3.83 \times 10^{-8} \text{ M} \Rightarrow [\cdot OH] = 1.74 \times 10^{-11} \frac{\text{mol}}{\text{L}}$

$\Rightarrow [DCE] = 3.8 \times 10^{-8} \text{ M}$ converged

$[DCE] = 3.7 \mu\text{g/L}$ about 99.5% removed

We met the treatment objective! $[DCE] < 7 \mu\text{g/L}$

... too bad it's for the wrong contaminant....

(b) Estimate/calculate concentration of $[\cdot OH]$

$[\cdot OH] = 1.7 \times 10^{-11} \frac{\text{mol}}{\text{L}}$ from part (a). This is quite reasonable.

We expect $10^{-12} - 10^{-9} \frac{\text{mol}}{\text{L}}$. So $1.7 \times 10^{-11} \frac{\text{mol}}{\text{L}}$ is right in

the expected range.

3. continued

c) So how would we do on DCA?

Assume $[^{\bullet}\text{OH}] = 1.74 \times 10^{-11} \frac{\text{mol}}{\text{L}}$

$\therefore k_1^{\text{app}} = (1.74 \times 10^{-11} \frac{\text{mol}}{\text{L}})(1.1 \times 10^8 \frac{\text{L}}{\text{mol}\cdot\text{s}}) = 1.91 \times 10^{-3} \text{ s}^{-1}$
 $= 0.0019 \text{ s}^{-1}$

$\tau = \frac{V}{Q} = \frac{10 \text{ m}^3}{0.0063 \text{ m}^3/\text{s}} = 1586 \text{ s}$

$C_I = \frac{700 \mu\text{g/L}}{(98.96 \text{ g/mol})(10^6 \mu\text{g/g})} = 7.1 \times 10^{-6} \frac{\text{mol}}{\text{L}}$

$[\text{DCA}] = \frac{7.07 \times 10^{-6} \text{ mol/L}}{1 + (0.00191 \text{ s}^{-1})(1586 \text{ s})} = 1.8 \times 10^{-6} \frac{\text{mol}}{\text{L}}$

$[\text{DCE}] = 174 \mu\text{g/L}$

about 75% removal

We are not even close to meeting the treatment objective.

d) Compare DCE to DCA.

The system works much better for DCE than for DCA. Why?

Because the second-order reaction rate coefficient for DCE and $^{\bullet}\text{OH}$ is much higher than that for DCA and $^{\bullet}\text{OH}$. Why?

Because DCE has a C=C double bond that is easy for the hydroxyl radicals to attack. DCA has only single bonds, which are less susceptible to oxidation by $^{\bullet}\text{OH}$.

e) Re-think conc. of $^{\bullet}\text{OH}$.

The denominator of the equation for $[^{\bullet}\text{OH}]$ is $22780 \text{ s}^{-1} + k_p[R]$.

For DCE, $k_p[R] = (6.8 \times 10^9 \frac{\text{L}}{\text{mol}\cdot\text{s}})(3.8 \times 10^{-8} \text{ M}) = 260 \text{ s}^{-1}$

For DCA, $k_p[R] = (1.1 \times 10^8 \frac{\text{L}}{\text{mol}\cdot\text{s}})(1.8 \times 10^{-6} \text{ M}) = 200 \text{ s}^{-1}$

These are pretty close and are both very small compared to 22780 s^{-1} . Neither the DCE nor the DCA has much effect on $[^{\bullet}\text{OH}]$... the other chemicals in the water are more important. Therefore the answer from part c) is just about right, and there is no need to adjust part c).

3. continued

- Ⓟ If we built the system without catching the mistake...
... the client would be very unhappy! The client would be expecting 99.5% removal of the target contaminant, but would get only 75% removal of the contaminant. The treatment objective would not be achieved and there might be fines or penalties. We could try to increase P_{O_2} , or perhaps we could try to remove some of the DOC or HCO_3^- , but I think we'd be in trouble. Probably a multi-stage reactor is needed here.