

1. Treat 380 L/min of water with EDB

(a)  $C_I = 900 \text{ mg/L}$ ; which carbon is least expensive?

Calculate the usage rate,  $UR = C_I / q_{eq}$  and  $q_{eq} = K_F (C_I)^{1/n}$

For packed bed, carbon equilibrates with influent concentration

|                                               | A         | B         | C         |
|-----------------------------------------------|-----------|-----------|-----------|
| $q_{eq} \text{ (mg/g)}$                       | 44,199    | 27,858    | 13,732    |
| $UR \text{ (g GAC/m}^3 \text{ water)}$        | 20.36     | 32.31     | 65.54     |
| $\text{Cost (}\$ / \text{m}^3 \text{ water)}$ | $\$0.071$ | $\$0.097$ | $\$0.212$ |

Carbon A is least expensive when  $C_I = 900 \text{ mg/L}$ .

(b) ... but what if  $C_I = 100 \text{ mg/L}$ ?

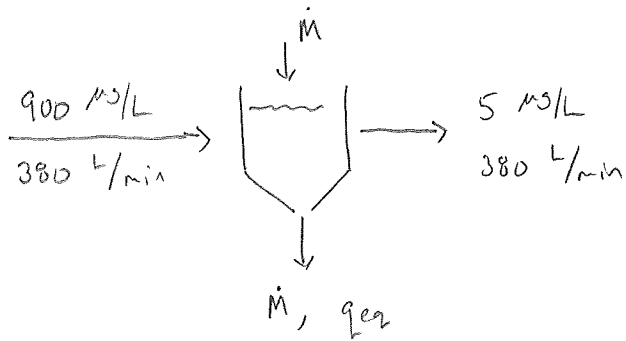
|                                               | A         | B         | C         |
|-----------------------------------------------|-----------|-----------|-----------|
| $q_{eq} \text{ (mg/g)}$                       | 6,199     | 5,958     | 4,449     |
| $UR \text{ (g GAC/m}^3 \text{ water)}$        | 16.13     | 16.79     | 22.48     |
| $\text{Cost (}\$ / \text{m}^3 \text{ water)}$ | $\$0.056$ | $\$0.050$ | $\$0.073$ |

Under the new condition, Carbon B is now less expensive.

As  $C_I$  gets lower, carbon B gets relatively better than carbon A because the  $1/n$  for carbon B is lower than the  $1/n$  for carbon A.

When  $C_I = 100 \text{ mg/L}$ , carbon A still has the lowest usage rate, but not the lowest cost ... the unit cost of B is lower than the unit cost of A, and the usage rates are similar, so overall, carbon B comes out ahead.

© Now use a CMFR with PAC instead



Recall that for this configuration, the carbon equilibrates with the effluent concentration!

By mass balance,  $UR = \frac{C_i - C_e}{q_{eq}}$  and  $q_{eq} = K_F (C_e)^{1/n}$

|                                                | A      | B      | C      |
|------------------------------------------------|--------|--------|--------|
| $q_{eq}$ ( $\mu\text{g/g}$ )                   | 426    | 727    | 957    |
| UR ( $\text{g GAC}/\text{m}^3 \text{ water}$ ) | 2102   | 1230   | 935    |
| cost ( $\$/\text{m}^3 \text{ water}$ )         | \$7.34 | \$3.68 | \$3.03 |

Wow, this type of treatment is much more expensive on a  $\$/\text{m}^3$  basis! It is over \$3.00 per  $\text{m}^3$  treated, whereas GAC for the same concentration was only \$0.07 per  $\text{m}^3$  treated. A big difference!

Anyway, now Carbon C is the least expensive. It has the lowest value of  $\frac{1}{n}$ , so as the relevant aqueous concentration gets lower, it gets relatively better.

④ Now what if  $C_I$  drops to 100 mg/L?

If we are using PAC in a CMFR, the influent concentration does not affect the relative order of the carbon. Continue using Carbon C as before.

Since  $q_{eq} = K_F (C_E)^{1/n}$ , if  $C_E$  does not change, then  $q_{eq}$  does not change. The usage rates in this problem will be lower than in part ③, but the order will not change.

|                                                     | A      | B      | C      |
|-----------------------------------------------------|--------|--------|--------|
| $q_{eq}$ (mg/g)                                     | 426    | 727    | 957    |
| $UR = \frac{C_I - C_E}{q_{eq}}$ (g/m <sup>3</sup> ) | 223    | 131    | 99.3   |
| cost (\$/m <sup>3</sup> water)                      | \$0.78 | \$0.39 | \$0.32 |

⑤ Explain/discuss.

In a packed bed reactor, which uses GAC, the carbon equilibrates with the influent aqueous concentration. Thus, a change in  $C_I$  can affect the relative performance of the carbon. However,

in a CMFR, which uses PAC, the carbon equilibrates with the effluent aqueous concentration. Thus, a change in  $C_I$  doesn't affect the relative performance (though it does impact overall cost).

If we were to change the treatment objective, then the opposite would be true -- a change in  $C_E$  would affect the relative performance of the PAC but not the GAC!

2. Treat water with 200  $\mu\text{g/L}$  EDB via air stripping

(a) Water flow rate and air flow rate

$$\text{Tower area } A = \pi d^2/4 = \left(\frac{\pi}{4}\right)(1.0 \text{ m})^2 = 0.785 \text{ m}^2$$

$$L_m = \frac{Q \rho}{A} \Rightarrow Q = \frac{L_m A}{\rho} = \frac{(10.0 \text{ kg/m}^2 \cdot \text{s})(0.785 \text{ m}^2)}{997 \text{ kg/m}^3}$$

$$Q = \underline{\underline{0.00788 \text{ m}^3/\text{s}}} = 125 \text{ gpm}$$

$$G_m = \frac{Q_a \rho}{A} \Rightarrow Q_a = \frac{G_m A}{\rho} = \frac{(0.50 \text{ kg/m}^2 \cdot \text{s})(0.785 \text{ m}^2)}{1.18 \text{ kg/m}^3}$$

$$Q_a = \underline{\underline{0.333 \text{ m}^3/\text{s}}}$$

(b) Henry's constant

$$H = \frac{P^{\text{sat}} / RT}{c^{\text{SL}}} = \frac{(1620 \text{ Pa}) / \left[ (8.314 \frac{\text{Pa} \cdot \text{m}^3}{\text{mol} \cdot \text{K}}) (298.15 \text{ K}) \right]}{(0.0234 \text{ mol/L})(1000 \text{ L/m}^3)}$$

$$\underline{\underline{H = 0.028}}$$

(c) Stripping factor

$$S = \left( \frac{Q_a}{Q} \right) (H) = \left( \frac{0.333 \text{ m}^3/\text{s}}{0.00788 \text{ m}^3/\text{s}} \right) (0.02793) = \underline{\underline{1.18}}$$

(d) Estimate HTU

$$HTU = \frac{Q/A}{K_L a} \quad \text{so we need } K_L$$

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{k_c H}$$

$$\frac{1}{K_L} = \frac{1}{2.2 \times 10^{-4} \text{ m/s}} + \frac{1}{(1.0 \times 10^{-2} \text{ m/s})(0.028)} \Rightarrow K_L = 1.23 \times 10^{-4} \frac{\text{m}}{\text{s}}$$

$$HTU = \frac{(0.00788 \text{ m}^3/\text{s}) / (0.785 \text{ m}^2)}{(1.23 \times 10^{-4} \text{ m/s})(58 \text{ m}^2/\text{m}^3)} = \frac{0.01004 \text{ m/s}}{0.00715 \text{ 1/s}}$$

HTU = 1.4 m ... ok if you wrote 1.40 m or 1.41 m  
any more than that would be excessive digits

(e) Estimate  $C_E$

We know  $L = NTU \times HTU$

$$8.0 \text{ m} = NTU \times 1.4 \text{ m} \Rightarrow NTU = 5.70$$

Also  $NTU = \frac{S}{S-1} \ln \left[ \frac{1 + (C_0/C_E)(S-1)}{S} \right]$  ... solve for  $\frac{C_0}{C_E}$ !

$$S \exp \left[ \frac{(S-1) NTU}{S} \right] = 1 + \left( \frac{C_0}{C_E} \right) (S-1)$$

$$\frac{C_0}{C_E} = \frac{S \exp \left[ \frac{(S-1) (NTU)}{S} \right] - 1}{S-1}$$

$$\frac{C_0}{C_E} = \frac{(1.18) \exp \left[ \frac{0.18}{1.18} (5.70) \right] - 1}{0.18} = 10.08$$

$$C_E = \frac{C_0}{10.08} = 19.8 \text{ mg/L} \approx \underline{\underline{20 \text{ mg/L}}} \quad \underline{\underline{90\% \text{ removal}}}$$

f) Did we achieve the objective?

We did not achieve the objective, because the stripping factor is too low,  $S=1.18$ . We should turn up the air flow rate to increase the stripping factor, thus improving removal from the water. The pressure drop is not currently too high, so probably it's fine to turn up the air flow rate. You could build a taller tower, but that sounds a lot more expensive than just turning up the air flow rate. Let's see what air flow rate would work:

$$L = 8.0 \text{ m} = \text{NTU} * \text{HTU}$$

If we assume that turning up the air doesn't affect HTU, then

$$8.0 \text{ m} = \text{NTU} (1.4 \text{ m}) \Rightarrow \text{NTU} = 5.70 \text{ as before}$$

$$5.70 = \frac{S}{S-1} \ln \left[ \frac{1 + \left( \frac{200 \text{ } \mu\text{g/L}}{5 \text{ } \mu\text{g/L}} \right) (S-1)}{S} \right]$$

Hmm, it is not possible to solve this in a timed exam unless you have a very fancy calculator. But I used Excel to find out that  $S=2.2$  will do the trick.

So increase the air flow rate from  $0.333 \frac{\text{m}^3}{\text{s}}$  to  $0.621 \frac{\text{m}^3}{\text{s}}$  and we should achieve our objective.

You'd have to double-check the pressure drop, but probably it will be fine.

In the context of a timed exam, I'd be looking for "increase the air flow rate," and preferably you'd try a value of  $Q_a$  or  $S$  to see what  $C_E$  it gives you. That would be do-able, even if solving for the particular  $Q_a$  and  $S$  is not feasible in a timed exam.

3. Treat water with 200  $\mu\text{g/L}$  EDB via AOP

(a) Estimate  $k_2$  for reaction of EDB with  $\cdot\text{OH}$ .

$$\text{CMFR} = \frac{C_E}{C_I} = \frac{1}{1+k_1\tau} \Rightarrow 0.50 = \frac{1}{1+k_1(15\text{ min})}$$

$$k_1 = 0.067 \text{ min}^{-1} = 1.1 \times 10^{-3} \text{ s}^{-1}$$

And  $k_1 = k_2 [\cdot\text{OH}]$ , and we're given  $[\cdot\text{OH}] = 4.0 \times 10^{-12} \frac{\text{mol}}{\text{L}}$

$$1.1 \times 10^{-3} \text{ s}^{-1} = k_2 (4.0 \times 10^{-12} \frac{\text{mol}}{\text{L}})$$

$$\underline{\underline{k_2 = 2.8 \times 10^8 \frac{\text{L}}{\text{mol}\cdot\text{s}}}} \quad \dots \text{ ok if you said } 2.78 \times 10^8 \frac{\text{L}}{\text{mol}\cdot\text{s}}$$

(b) Estimate effluent EDB conc. if  $K_L a$  doubles

$$\text{Use } [\cdot\text{OH}] = \frac{(K_L a) \{ P_{\text{O}_3} / H_{\text{PL}} - [\text{O}_3] \}}{\{ k_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2] + k_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2] + k_{\text{HCO}_3} [\text{HCO}_3^-] + k_{\text{NOM}} [\text{NOM}] + k_{\text{R}} [\text{R}] \}}$$

Equation 18-48 from text or from class notes.

Now we double  $K_L a$

So if nothing else changes,  $[\cdot\text{OH}]$  also doubles.

$$\text{Thus } [\cdot\text{OH}] = 8.0 \times 10^{-12} \frac{\text{mol}}{\text{L}}$$

$$k_1 = [8.0 \times 10^{-12} \frac{\text{mol}}{\text{L}}] [2.78 \times 10^8 \frac{\text{L}}{\text{mol}\cdot\text{s}}] = 2.22 \times 10^{-3} \text{ s}^{-1} \\ = 0.133 \text{ min}^{-1}$$

$$\frac{C_E}{C_I} = \frac{1}{1 + (0.133 \text{ min}^{-1})(15 \text{ min})} = 0.333$$

$$\underline{\underline{C_E = 67 \mu\text{g/L}}} \quad \text{if } K_L a \text{ doubles}$$

Aside #1

Not required as part of your answer!  
Just wondering...

Question 3, Aside #1:

This is not necessary to answer the questions on the test, but I am curious: do all the data given in the problem agree with the text equation 18-48?

$$[\text{OH}^-] = \frac{(K_{La})_{\text{O}_3} \{ P_{\text{O}_3} / H_{\text{O}_3} - [\text{O}_3] \}}{k_9 [\text{HO}_2^-] + k_{10} [\text{H}_2\text{O}_2] + k_{\text{HCO}_3} [\text{HCO}_3^-] + k_{\text{NO}_3} [\text{NO}_3^-] + k_R [R]} \quad (18-48)$$

$$\begin{aligned} \text{Numerator: } & (4.0 \times 10^{-4} \text{ s}^{-1}) \left[ \frac{0.040 \text{ atm}}{89.1 \frac{\text{atm} \cdot \text{L}}{\text{mol}}} - (2.7 \times 10^{-5} \frac{\text{mol}}{\text{L}}) \right] \\ & = 1.688 \times 10^{-7} \frac{\text{mol}}{\text{L} \cdot \text{s}} \end{aligned}$$

Denominator: I'll assume it's OK to ignore  $k_{10} [\text{H}_2\text{O}_2]$  at  $\text{pH} = 7$ , but we'll consider the other four terms

$$\begin{aligned} & \underbrace{(2.7 \times 10^7 \frac{\text{L}}{\text{mol} \cdot \text{s}})(5.0 \times 10^{-5} \frac{\text{mol}}{\text{L}})}_{\text{H}_2\text{O}_2} + \underbrace{(8.5 \times 10^6 \frac{\text{L}}{\text{mol} \cdot \text{s}})(3.0 \times 10^{-3} \frac{\text{mol}}{\text{L}})}_{\text{HCO}_3^-} + \underbrace{(3.9 \times 10^8 \frac{\text{L}}{\text{mol} \cdot \text{s}})(2.0 \times 10^{-5} \frac{\text{mol}}{\text{L}})}_{\text{NO}_3^-} \\ & + \underbrace{(2.8 \times 10^8 \frac{\text{L}}{\text{mol} \cdot \text{s}})(100 \frac{\text{mg}}{\text{L}})(\frac{1 \text{ g}}{10^6 \text{ mg}})(\frac{1 \text{ mol}}{187.86 \text{ g}})}_{\text{EDB}} \end{aligned}$$

$$\text{Denominator} = 34,800 \text{ s}^{-1}$$

$$[\text{OH}^-] \stackrel{?}{=} \frac{1.688 \times 10^{-7} \text{ mol}/(\text{L} \cdot \text{s})}{34,800 \text{ s}^{-1}} \Rightarrow [\text{OH}^-] = 4.85 \times 10^{-12} \frac{\text{mol}}{\text{L}}$$

It's pretty close to the reported value of  $4.0 \times 10^{-12} \frac{\text{mol}}{\text{L}}$ .

The discrepancy is that (18-48) doesn't include a term  $-\frac{Q}{V}([\text{O}_3]_2 - [\text{O}_3])$  in the numerator, which I included in my "modified" 18-48.

If we include that term then everything agrees!



Now back to our problem...

© What would be  $C_E$  for EDB if we remove most of the  $\text{HCO}_3^-$ ?

Under the conditions originally given, the denominator of the equation for  $[\text{OH}^-]$  is:

$$\begin{aligned} \text{denominator} &= k_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2] + k_{\text{HCO}_3^-} [\text{HCO}_3^-] + k_{\text{NOM}} [\text{NOM}] + k_p [\text{EDB}] \quad \left. \begin{array}{l} \text{if we ignore} \\ \text{H}_2\text{O}_2^- \\ \text{at pH}=7 \end{array} \right\} \\ \text{denom} &= (2.7 \times 10^7 \frac{\text{L}}{\text{mol}\cdot\text{s}}) (5.0 \times 10^{-5} \frac{\text{mol}}{\text{L}}) + (8.5 \times 10^6 \frac{\text{L}}{\text{mol}\cdot\text{s}}) (3.0 \times 10^{-3} \frac{\text{mol}}{\text{L}}) \\ &\quad + (3.9 \times 10^8 \frac{\text{L}}{\text{mol}\cdot\text{s}}) (2.0 \times 10^{-5} \frac{\text{mol}}{\text{L}}) + (2.78 \times 10^8 \frac{\text{L}}{\text{mol}\cdot\text{s}}) (100 \frac{\mu\text{g}}{\text{L}}) (\frac{1 \text{ mol}}{187.86 \times 10^6 \mu\text{g}}) \end{aligned}$$

$$\begin{aligned} \text{denom} &= \underbrace{1350 \text{ s}^{-1}}_{\text{H}_2\text{O}_2} + \underbrace{25,500 \text{ s}^{-1}}_{\text{HCO}_3^-} + \underbrace{7800 \text{ s}^{-1}}_{\text{NOM}} + \underbrace{148 \text{ s}^{-1}}_{\text{EDB}} \\ &= 34,800 \text{ s}^{-1} \end{aligned}$$

Then if we reduce  $[\text{HCO}_3^-]$  from  $183 \frac{\text{mg}}{\text{L}}$  to  $12.2 \frac{\text{mg}}{\text{L}}$ ,

or  $3.0 \times 10^{-3} \frac{\text{mol}}{\text{L}}$  to  $2.0 \times 10^{-4} \frac{\text{mol}}{\text{L}}$ ,

the  $\text{HCO}_3^-$  term of the denominator becomes  $1700 \text{ s}^{-1}$ ,

and the entire denominator becomes  $11,000 \text{ s}^{-1}$ , if we ignore changes to the other terms.

So  $[\text{OH}^-]$  increases by a factor  $\frac{34,800}{11,000} = 3.16!$

$$[\text{OH}^-] = (4.0 \times 10^{-12} \frac{\text{mol}}{\text{L}}) (3.16) = 1.27 \times 10^{-11} \frac{\text{mol}}{\text{L}}$$

$$\begin{aligned} k_2 [\text{OH}^-] &= k_1^{\text{eff}} = (2.78 \times 10^8 \frac{\text{L}}{\text{mol}\cdot\text{s}}) (1.27 \times 10^{-11} \frac{\text{mol}}{\text{L}}) = 0.00352 \text{ s}^{-1} \\ &= 0.211 \text{ min}^{-1} \end{aligned}$$

$$\frac{C_E}{C_I} = \frac{1}{1 + k_1 \tau} = \frac{1}{1 + (0.211 \text{ min}^{-1})(15 \text{ min})} = 0.24$$

$$\underline{\underline{C_E = 48 \mu\text{g/L for EDB}}}$$

(d) What happens to EDB conc. if we double  $P_{O_3}$ ?

Numerator of the expression for  $[OH]$  contains:

$$(K_L a)_{O_3} \left\{ \frac{P_{O_3}}{H_{PC}} - [O_3] \right\}$$

Under the original conditions,

$$\frac{P_{O_3}}{H_{PC}} - [O_3] = \frac{0.040 \text{ atm}}{89.1 \text{ L/atm}\cdot\text{mol}} - 2.7 \times 10^{-5} \frac{\text{mol}}{\text{L}} = 4.22 \times 10^{-4} \frac{\text{mol}}{\text{L}}$$

So if we double  $P_{O_3}$ , if  $[O_3]$  doesn't change much,

$$\frac{P_{O_3}}{H_{PC}} - [O_3] = \frac{0.080 \text{ atm}}{89.1 \text{ L/atm}\cdot\text{mol}} - 2.7 \times 10^{-5} \frac{\text{mol}}{\text{L}} = 8.71 \times 10^{-4} \frac{\text{mol}}{\text{L}}$$

So the  $[OH]$  concentration should increase by a factor  $\frac{8.71}{4.22} = 2.06$

$$[OH] = \left( 4.0 \times 10^{-12} \frac{\text{mol}}{\text{L}} \right) \left( \frac{8.71}{4.22} \right) = 8.256 \times 10^{-12} \frac{\text{mol}}{\text{L}}$$

$$k_1^{app} = \left( 2.78 \times 10^8 \frac{\text{L}}{\text{mol}\cdot\text{s}} \right) \left( 8.256 \times 10^{-12} \frac{\text{mol}}{\text{L}} \right) = 0.0023 \text{ s}^{-1} = 0.1377 \text{ min}^{-1}$$

$$\frac{C_E}{C_I} = \frac{1}{1 + (15 \text{ min})(0.1377 \text{ min}^{-1})} = 0.3262$$

$$\underline{\underline{C_E = 65 \frac{\text{M}}{\text{L}} \text{ for EDB}}}$$

COMMENT: In parts b, c, and d, while I was estimating the effects of the proposed changes, I assumed that other conditions in the reactor would remain unchanged. We know this isn't true. For instance, in part d, I assumed  $[O_3]$  would stay at  $2.7 \times 10^{-5} \frac{\text{mol}}{\text{L}}$  even when  $P_{O_3}$  increases -- really,  $[O_3]$  would increase some, meaning that my estimate of  $65 \text{ M/L}$  is a bit too optimistic. But in the context of a timed exam, this is a decent approximation. More refined estimates would require iterative calculations.

② Which process change gives the best improvement?

The best improvement comes from removing  $\text{HCO}_3^-$ . Doubling  $K_L a$  or doubling  $P_{\text{O}_3}$  would roughly double  $[\cdot\text{OH}]$  and hence double  $k_1^{\text{app}}$ .

But removing  $\text{HCO}_3^-$  more than triples  $[\cdot\text{OH}]$  so gives the best result.

This is because  $\text{HCO}_3^-$  is the species that most strongly quenches the  $\cdot\text{OH}$  radicals. Removing  $\text{HCO}_3^-$  can greatly reduce the quenching, hence giving a big boost to our removal of EDB.

Aside #2

To see how close these estimates came, I ran my iterative Excel spreadsheet for the conditions of this problem. Here were the results.

Doubling  $K_L a$ : I predicted  $C_E = 67 \frac{\text{M}}{\text{L}}$ , actually  $C_E = 77 \frac{\text{M}}{\text{L}}$ .

Why? Because when  $K_L a$  increases,  $[\text{O}_3]$  increases, which is the idea -- but if we look at  $(K_L a)(P/A - [\text{O}_3])$ , it shows us that doubling  $K_L a$  won't fully double  $[\cdot\text{OH}]$ . In the end, doubling  $K_L a$  only increases  $[\cdot\text{OH}]$  by a factor of about 1.6.

Removing  $\text{HCO}_3^-$ : I predicted  $C_E = 48 \frac{\text{M}}{\text{L}}$ , actually  $C_E = 22 \frac{\text{M}}{\text{L}}$ !

Why? When we reduce  $[\text{HCO}_3^-]$ , we increase  $[\cdot\text{OH}]$ , as planned. But the increase in  $[\cdot\text{OH}]$  then removes some of the NOM, too. So then the quenching reduces even further! Thus the final  $[\cdot\text{OH}]$  increases by more than the factor 3.16 that I had estimated.

Doubling  $P_{\text{O}_3}$ : I predicted  $C_E = 65 \frac{\text{M}}{\text{L}}$ , actually  $C_E = 75 \frac{\text{M}}{\text{L}}$ .

This one is basically the same as doubling  $K_L a$ .

So my predicted #s follow the correct trend in terms of which method is best or worst, even though the particular numbers aren't perfect.