

ENV 6519: Physical & Chemical Processes for Groundwater Remediation

Spring 2021
Homework #5
Due Thursday, February 18, 2021 (probably)

University of South Florida
Civil & Environmental Engineering
J.A. Cunningham

On homework #4 this semester, you estimated how long it would take TCE to break through a packed bed of granular activated carbon. When you did that, I gave you a value for the length of the mass-transfer zone, L_{MTZ} . In general, you would not know *a priori* the length of the mass-transfer zone. Furthermore, the mass-transfer zone might not actually be S-shaped and symmetric as we assumed. Luckily for us, a paper by Hand et al. [1984] describes a method by which you can estimate the shape and the length of the mass-transfer zone, and therefore come up with some better estimates than those you derived in homework #4.

Hand DW, Crittenden JC, Thacker WE, 1984. Simplified models for design of fixed-bed adsorption systems. *Journal of Environmental Engineering (ASCE)*, 110(2), 440–456.

This method is also described in section 15-6 of your text, in the sub-section labeled “Modeling GAC Performance.”

As a reminder, here is the problem we’re solving:

You need to treat a contaminated groundwater stream that is being pumped out of the ground at a rate of $0.40 \text{ m}^3/\text{min}$. The groundwater contains 1.0 mg/L of TCE, which you must reduce to $5 \text{ }\mu\text{g/L}$. You will use granular F400 activated carbon in a fixed bed. According to Speth and Miltner [1990], the isotherm for the adsorption of TCE from Ohio River water onto F400 carbon is: $q_e = 1180 (C_{eq})^{0.484}$ where q_e is given in $\mu\text{g/g}$ and C_{eq} is given in $\mu\text{g/L}$. Here are some parameters and conditions that you will use for your design.

Influent concentration, $C_I = 1.0 \text{ mg/L}$	GAC grain diameter, $d_p = 1.0 \text{ mm}$
Allowable effluent conc., $C_E = 5 \text{ }\mu\text{g/L}$	GAC grain internal porosity, $\varepsilon_p = 0.6$
Flow rate, $Q = 0.40 \text{ m}^3/\text{min}$	Intergranular porosity of bed, $\varepsilon = 0.4$
Bed length, $L = 4.0 \text{ m}$	Bulk density of carbon in the bed, $\rho_f = 480 \text{ kg/m}^3$
Superficial velocity, $v_0 = 10.0 \text{ m/hr}$	Temperature, $T = 18 \text{ }^\circ\text{C}$

Also assume that the sphericity of the carbon grains (which you did not need in HW 4) is $\phi = 0.7$.

As you will see when you read the paper, Hand et al. [1984] used the inter-granular porosity (ε) in their calculations, and some of their equations depend on that porosity. I try to avoid calculations that depend on porosity, because it is often unclear if we should use ε , ε_{tot} , or

something in between. However, for the purposes of this assignment, use the inter-granular porosity ε in order to be consistent with Hand et al. The effect of using ε instead of ε_{tot} should, hopefully, be small. (In essence, Hand et al. ignored intra-granular porosity, which we know can be significant; but this assumption probably won't throw off the final results too much. I hope.)

I *strongly* recommend that you set up an Excel spreadsheet or a Matlab program to handle the following calculations. It will make your life much easier, especially when you get to problem 2.

1. (65 pts)

- a. Calculate the empty bed contact time, EBCT, in minutes. Also calculate θ_m , the theoretical number of bed volumes treated before the midpoint of the breakthrough curve. Finally, calculate (C_1/q_{eq}) , the theoretical minimum carbon usage rate.
- b. Use the Hayduk-Laudie method to estimate D_{TCE} , the diffusivity of TCE in water, at the temperature given (18 °C).
- c. Estimate the mass transfer coefficient, k_L , for the mass transfer of TCE from the bulk water to the surface of the activated carbon grain. Use the Gnielinski correlation given in your text book on p 423. Report k_L in units of m/s. CAREFUL: On page 423, the notation ρ_f is used to mean the *fluid* density, not the *carbon* density.

[Note: I did this problem with a different correlation for k_L , and I am curious to see how closely they agree. My correlation came from McCabe WL, Smith JC, Harriott P, 1985; *Unit Operations of Chemical Engineering*, 4th edition; McGraw-Hill, New York, NY; p 604:

$$k_L = 1.17 \frac{D_{\text{TCE}}}{d_p} (\text{Re})^{0.585} (\text{Sc})^{1/3}$$

$$\text{Re} = \frac{\rho_{\text{water}} v_0 d_p}{\mu_{\text{water}}} \quad \text{Sc} = \frac{\mu_{\text{water}}}{\rho_{\text{water}} D_{\text{TCE}}}$$

where ρ_{water} is the density of water, d_p is the GAC particle diameter, and μ_{water} is the viscosity of water.]

- d. Based on your calculated value of Re, do you think the flow through the pressure vessel is laminar, turbulent, or somewhere in between? Is this what you would expect, i.e., does it seem reasonable? Explain briefly (a sentence or two).

problem 1 continues →

1. continued

- e. Estimate the effective diffusion coefficient, D_{eff} , for TCE to diffuse into the grains of carbon. Assume that TCE diffusion in the grains is controlled by pore diffusion, retarded by the adsorption process. Use the following relationship to estimate D_{eff} :

$$D_{\text{eff}} = 3.72 \frac{D_{\text{TCE}} \varepsilon_p C_I}{\chi \rho_a q_{\text{eq}}} \quad \text{where } D_{\text{TCE}} \text{ means the aqueous diffusivity of TCE}$$

where χ is the tortuosity of the pore, which you can here assume to be 1 for simplicity, and ρ_a is the apparent density of the grain of carbon (mass of carbon per volume of grain). If you look carefully, this equation is similar to what we had in the lecture notes when we were considering intra-granular pore diffusion. Report D_{eff} in units of m^2/s .

- f. From your estimates of k_L and D_{eff} , estimate the Biot number (Bi):

$$Bi = \frac{1}{\phi} \frac{C_I}{\rho_a q_{\text{eq}}} \frac{k_L / r_p}{D_{\text{eff}} / r_p^2}$$

where r_p is the radius of the carbon grain, i.e., half of d_p . This equation is equivalent to eqn 10 from Hand et al. [1984]; see also Table 15-15 with equation 15-155 in your text. For your conditions, is $Bi > 0.5$? This is a criterion for validity of the numerical solution method of Hand et al. (though apparently we can get within 10% error even if $Bi < 0.5$).

- g. Using Figure 2 or Table 1 from Hand et al. [1984] -- or Figure 15-28 in your text -- estimate the minimum Stanton number, St_{min} , that would result in validity of the constant-pattern assumption.
- h. Use St_{min} to estimate the minimum column length that is required for the constant pattern to be established:

$$L_{\text{min}} = St_{\text{min}} \frac{\phi}{(1 - \varepsilon)} \frac{v_0}{(k_L / r_p)}$$

Is our column long enough to provide sufficient travel time for the constant pattern to be established?

problem 1 continues →

1. continued

- i. Estimate the Stanton number,

$$St = \frac{1 - \varepsilon}{\varepsilon} \frac{1}{\phi} \frac{k_L / r_p}{v_0 / (\varepsilon L)} \quad (\text{equivalent to eqn 11 from Hand et al.})$$

This equation is equivalent to equation 11 from Hand et al. [1984]; see also Table 15-15 and equation 15-153 in your text. For your conditions, is $St > St_{\min}$, such that the constant-pattern assumption is valid? (Hint: your answers to parts h and i should be consistent.)

- j. Based on the values of Bi and $(1/n)$, estimate the coefficients A_0, A_1, A_2, A_3 , and A_4 from the paper of Hand et al. [1984]. Then, use these coefficients in the formula

$$T = 1 + \left\{ \left[A_0 + A_1 X^{A_2} + \frac{A_3}{1.01 - X^{A_4}} \right] - 1 \right\} \frac{St_{\min}}{St}$$

where X is normalized concentration, C/C_1 . Use this to find the values of T that correspond to normalized concentrations of 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 0.95, and 0.99. The calculated (X, T) points will give you the breakthrough curve after just a few more manipulations.

- k. Convert the values of T that you calculated above to units of empty bed volumes treated. This is easily done by $\theta = \theta_m * T$, and you already calculated θ_m . Then, graph the breakthrough curve from the beginning of an adsorption run until the adsorbent bed is exhausted. Graph your breakthrough curve as normalized effluent concentration, C_E/C_1 (on the y-axis), versus number of empty bed volumes treated, θ (on the x-axis).
- l. Estimate the length of the mass-transfer zone, L_{MTZ} , in meters. Calculate this as the distance between the point at which $C/C_1=0.01$ and the point at which $C/C_1=0.99$. Hint: you know the values of θ that correspond to these values of C/C_1 ...use the θ values to calculate the distances you need. (It is possible to derive a relationship between $\Delta\theta$ and L_{MTZ} ...some years, I work this out in class, so check your notes.)
- m. At approximately what time is the allowable effluent concentration exceeded? Based on this, estimate the usage rate of carbon, i.e., the mass of carbon required per volume of water treated. Report the usage rate in units of g/m^3 .
- n. The simpler method that you used in homework 4 would predict that $C/C_1 = 0.5$ after θ_m bed volumes. Using the more sophisticated approach of Hand et al. [1984], how many bed volumes are treated before $C/C_1 = 0.5$? How closely do these two estimates agree?

2. (20 pts) Repeat problem #1, parts (e)–(n), but this time use a lower value of the effective diffusion coefficient. Use

$$D_{\text{eff}} = 0.4 \frac{D_{\text{TCE}} \epsilon_p C_I}{\chi \rho_a q_{\text{eq}}}$$

which might correspond to diffusion *hindered by natural organic matter* present in the water.

Hint #1: if you did problem #1 in a spreadsheet, you can copy that sheet and then just change the parts of the sheet that require modification. It's not painful; I did it to make sure.

Hint #2: If you find that $St < St_{\text{min}}$, then set $St_{\text{min}} = St$ for part (j) of the problem...that allows you to proceed without introducing very much error. In fact, if you wish, you can use Figure 2(b) of the Hand paper to verify that less than 10% error is introduced by this approximation (optional, not required for this assignment).

3. (15 pts)
- Compare the results from problem #2 to those from problem #1. What happened to the length of the mass-transfer zone, L_{MTZ} , when we accounted for hindered pore diffusion? What do you conclude about the effect that internal diffusion rate has on the length of the mass-transfer zone? What effect did this have on the time at which the effluent standard is exceeded? What about the carbon usage rate? On a percentage basis, how much did the carbon usage rate change from problem (1) to problem (2)?
 - Let's think about what all this means. On homework #4, you used a relatively simple method to estimate the TCE breakthrough and carbon usage rate. Here in homework #5, you used the more sophisticated approach of Hand et al. [1984] to get more precise estimates. Do you think the "simple" method is good enough, or do you think the more sophisticated "Hand" approach is needed? For instance, when you complete your design project this semester, which method would you recommend? Briefly explain your reasoning.