

ENV 6519: Physical & Chemical Processes for Groundwater Remediation

Spring 2021
Homework #4
Due Thursday, Feb. 11, 2021

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Civil & Environmental Engineering
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1. (45 pts) (*adapted from a problem written by Prof Paul Roberts of Stanford University*)
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 $5 \text{ }\mu\text{g/L}$. For this problem, you will use powdered F400 activated carbon (i.e., PAC). 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 $\mu\text{g/L}$. The treatment will be carried out in a completely mixed flow reactor (CMFR; same as CSTR for the chemical engineers) that has an average hydraulic residence time of 2.0 hours.
- (9 pts) Calculate the dose rate of PAC required to achieve the TCE treatment objective. Give your answer in units of grams of PAC required per m^3 of water treated. Assume that equilibrium is obtained within the average hydraulic residence time of 2.0 hours.
 - (13 pts) Calculate the required activated carbon dose rates if a two-stage CMFR is used instead of a single-stage CMFR. Report your answer as grams of PAC required (total for both reactors) per m^3 of water treated. Each of the two stages has an average hydraulic residence time of 2.0 hours. Assume that carbon is added at equal rates to the two contactors, and that equilibrium is reached within the time of 2 hours. Also assume that the carbon is completely separated from the water between the two stages (probably not realistic, but OK for here). Hint: two equations for two unknowns.
 - (5 pts) Discuss the difference in carbon usage rate (i.e., the g of carbon required per m^3 water treated) for parts (a) and (b). Which scheme is more efficient in terms of carbon usage rate? Why?
 - (9 pts) Evaluate the assumption, made in parts (a) and (b), that equilibrium is reached within 2 hours. Assume that the PAC grain diameter is $50 \text{ }\mu\text{m}$, the internal void fraction is $\varepsilon_p = 0.60$, and the grain density is $\rho_a = 0.8 \text{ g of carbon per cm}^3$ of grain volume. The (unretarded) diffusivity of TCE in water-filled pores is $0.86 \times 10^{-9} \text{ m}^2/\text{sec}$ (estimated from Hayduk-Laudie). About how long should it take for the PAC to equilibrate with the water? Is the assumption of equilibrium within 2 hours valid?

problem 1 continues →

1. continued

- e. (9 pts) Spoiler alert: in part (d) you should have found that equilibrium is **not** reached within 2 hours. Therefore, let's now modify our answer to part (a) to account for the non-equilibrium. Use equation 15-58 of your text to estimate a dimensionless time \bar{t} corresponding to the residence time of 2 hr. For your calculation, don't use a surface diffusion coefficient D_s , because in ENV 6519 we adopt a pore-diffusion model instead of a surface-diffusion model. Therefore, in your calculation, use an effective pore diffusion coefficient (such as you might have used in part (d)). Once you have your value of \bar{t} , use equations 15-99 and 15-59 to estimate the average adsorbed concentration q that you will actually achieve in the reactor. (Hint: it should be lower than the q you used in part (a)). From there, you can update your estimate of how much PAC is needed (for the single-reactor case, not the two-reactor case). What is the new usage rate? Compare it to your value from part (a). How much does the usage rate increase because of the non-equilibrium? Do you think an assumption of equilibrium is OK, or must we account for the non-equilibrium?

2. (45 pts) (*adapted from a problem written by Prof Paul Roberts of Stanford University*)

Now let's treat that same waste stream (from problem 1) with granular activated carbon (GAC) in a fixed bed, instead. You will use granular F400 activated carbon. 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, $\epsilon_p = 0.60$
Flow rate, $Q = 0.40 \text{ m}^3/\text{min}$	Intergranular porosity of bed, $\epsilon = 0.40$
	Bulk density of carbon in the bed, $\rho_f = 480 \text{ kg/m}^3$

For simplicity, assume that the mass-transfer zone is S-shaped and symmetrical with a constant length $L_{MTZ} = 2.0 \text{ m}$. (In homework #5, we will examine a more sophisticated method of dealing with the length and the shape of the mass-transfer zone.)

- a. (5 pts) Suppose we design our GAC pressure vessel to have a superficial velocity $v_0 = 10.0 \text{ m/hr}$. That is a pretty typical value in practice. Then, what is the required cross-sectional area of the pressure vessel? What is the required diameter? If the required diameter is greater than about 6 m, then it is probably necessary to split the flow into two (or more) contactors in parallel; is that required here, or is one contactor sufficient?

problem 2 continues →

2. continued

- b. (5 pts) It has been proposed that the length of your GAC adsorber should be 4.0 m. Given this length, what is the empty-bed contact time (EBCT) of the contactor? Do you find that it is within the typical design range of 5–30 min? If it is not, what length do you recommend to ensure that the EBCT falls within the recommended range?
- c. (5 pts) Suppose that all of the column porosity (both inter-granular and intra-granular porosity) is accessible for flow. Under this assumption, what would be the residence time (in minutes) of a non-sorbing conservative tracer in the adsorbent bed? Now suppose that only the inter-granular porosity (none of the intra-granular) is accessible for flow. Then what would be the residence time (in minutes) of the non-sorbing conservative tracer? The actual time probably lies somewhere between these two extremes. Typical values in practice might be in the range 2–10 min.
- d. (5 pts) Now let's go back to considering TCE. Calculate θ_m , the number of bed volumes that can be treated before the midpoint of the mass-transfer zone breaks through the column.
- e. (5 pts) Based on the assumed length of the adsorption zone, calculate θ_{br} (the number of bed volumes before the onset of breakthrough) and θ_{ex} (the number of bed volumes before the carbon is completely exhausted).
- f. (5 pts) Sketch a 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_I (on the y-axis), versus number of empty bed volumes treated, θ (on the x-axis). Make your graph semi-quantitative based on the values of θ_{br} , θ_m , and θ_{ex} that you calculated in part (d).
- g. (5 pts) Approximately how many bed volumes of water can be treated before the effluent concentration exceeds the allowable effluent standard of 5 $\mu\text{g/L}$? Does it fall within the expected range of 3,000–30,000 bed volumes? How long a time (in days) does this represent? Does it fall within the typical range of 100–600 days? If your estimated values do not fall within the expected ranges, what do you think is causing the discrepancy?
- h. (5 pts) From your answer to part (g), calculate the rate at which carbon must be replaced or regenerated. Express your answer in units of g GAC per m^3 of water treated, i.e., as a usage rate (UR).
- i. (5 pts) Calculate the sorbed concentration (q_{eq}) that is in equilibrium with the water at the influent concentration of 1.0 mg/L. Report your answer in units of mg/g. Then, calculate the ratio C_I/q_{eq} in units of g GAC per m^3 water. This would be the usage rate if the adsorption zone were infinitesimally thin. Compare this value to the usage rate that you found in part (h). Does the length of the mass-transfer zone have a significant effect on the usage rate?

3. (10 pts) Compare the GAC usage rate from problem 2(h) to the PAC dose rates from problems 1(a), 1(b), and 1(e). Do you consider there to be a substantial difference in carbon use rate for GAC versus PAC? Which one represents a more efficient use of the carbon? Why? (i.e., explain the underlying cause for the difference in efficiency) Suppose you were planning on treating a contaminated groundwater stream continuously for a period of approximately 15 years (as in your design project this semester). Which would you use, PAC or GAC? Why?