Fate & Transport of Chemicals in the Environment

Homework #8 University of South Florida
Due Monday, April 4, 2022 Prof J A Cunningham

Answer questions 1–3 (total of 40 points for the three problems)

1. In class I told you that the exit-age distribution function for a CMFR is $E(t) = (1/\tau)\exp(-t/\tau)$. Let's make sure this holds up to scrutiny.

   a. Verify that $\int_0^\infty E(t)dt = 1$.

   b. Verify that $\int_0^\infty t\, E(t)dt = \tau$.

   By the way, part (a) is basically the same thing as showing that $\int_0^\infty Q\, C_E(t)\, dt = M$ for a CMFR in response to a pulse input of tracer, i.e., for $C_E(t) = (M/V)\exp(-t/\tau)$. I had threatened to make you verify that, for an ideal CMFR responding to a pulse input, $\int_0^\infty Q\, C_E(t)\, dt = M$. But now I don't have to make you do it, because you are essentially doing the same thing in part (a) of this problem. The math is the same.

2. Consider a chemical undergoing first-order degradation in a CMFR at steady state. The influent concentration is C_I. Use the segregated flow model to derive a formula for the ratio C_E/C_I. How does the result compare to the formula for C_E/C_I that we previously derived using a mass balance?

   (Interestingly, this works well for first-order reaction kinetics, but it doesn't actually work well for other reaction order. It is not clear to me why not. To me, it seems like it should work for *any* reaction order, but it doesn't. I have been puzzling over that for a while. Some text books discuss it, but not in a way that has made clear to me why it doesn't work.)

3. Consider a well-mixed reservoir with a volume $V = 5000\ m^3$. Water enters and exits the reservoir at a rate $Q = 2.5\ m^3/min$. At time $t = 0$, a 50-kg slug of conservative tracer is added very rapidly to the reservoir's inlet. Other than the rapid pulse input, there is no input of tracer into the reservoir (i.e., the inlet stream is "clean").

   a. Estimate/calculate τ, the average hydraulic residence time in the reservoir.

   b. Estimate/calculate C_0, the concentration of tracer in the reservoir immediately after the pulse is added.

problem 3 continues →

3. continued

   c. Write the expression for the concentration of tracer in the reservoir effluent, $C_E(t)$. Then make a graph of $C_E(t)$ versus time.

   d. How much time does it take for 95% of the added tracer to be washed out of the reservoir? How much time does it take for 99% of the mass to be washed out? Report these answers both in units of minutes and in normalized dimensionless time, t/τ.

   The answer to part (d) is a well-known result in reactor theory. It takes about 3 residence times to flush out 95% of the mass from a CMFR and it takes about 5 residence times to flush out 99%. Hopefully you got results close to these.

Now pick three of the following five problems.
You must choose *at least one* of problems 4 and 5.

4. (20 pts) In class, we considered the problem of first-order degradation in a plug flow reactor (PFR) at steady state. Thinking of the PFR as a "batch reactor on a conveyor belt," we argued that the effluent concentration C_E is related to influent concentration C_I according to

   $C_E = C_I \exp(-k_1 \tau)$.

   I know that many of you were disappointed that we didn't use a mass balance to derive this result. Let's rectify that now. We will re-derive this result using a mass balance. I will walk you through it.

- Consider a plug-flow reactor of length L and cross-sectional area A. Thus, the total volume of the PFR is $L*A$.
- Let's say that x is the longitudinal position in the PFR. The inlet to the PFR is at $x = 0$, and the exit from the PFR is at $x = L$.
- The concentration of our chemical varies throughout the length of the PFR. At $x = 0$, we know the concentration is C_I. Within the PFR, the concentration varies with position, i.e., C is a function of x. We can call it $C(x)$. We want to derive a formula for C at $x = L$ (i.e., at the PFR exit).
- The volumetric flow rate of water through the PFR is Q.
- The velocity of the water through the PFR is $v = Q/A$.
- Now consider a thin slice of the PFR that goes from x to $x + \Delta x$. It still has a cross-sectional area A, a volumetric flow rate Q, and a velocity v. But the length of the slice is only Δx, and the volume of the slice is only $A*\Delta x$.

   a. Draw a picture that summarizes the situation described above.

problem 4 continues →

4. continued

   b. *Write a mass balance for the mass of the degrading chemical, using your thin slice as a control volume*. Remember that we are dealing with first-order degradation at steady state. Hint: think carefully about the "flow in" and "flow out" terms in your mass balance. For one of the terms in your mass balance, you should have the volume of the slice as part of your expression; recall the volume of the slice is $A*\Delta x$.

   c. Re-arrange your mass balance from part (b) to derive an equation that says

$$\frac{C(x+\Delta x)-C(x)}{\Delta x}=\cdots$$

   d. Take the limit as Δx goes to zero. What happens to the left-hand side?

   e. Solve the differential equation from part (d). Hint: you know C at $x = 0$.

   f. Show that $C_E = C_I \exp(-k_1 \tau)$.

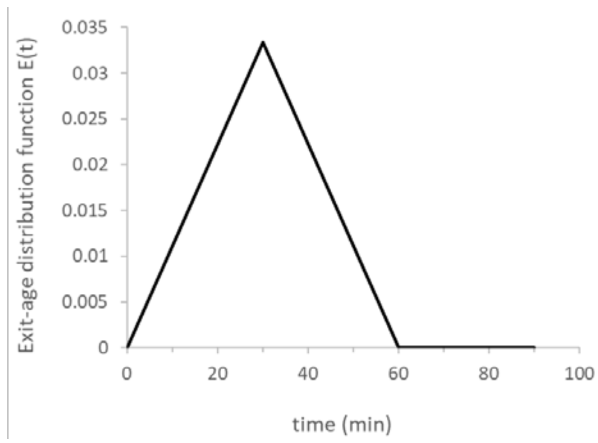
5. (20 pts) In class, we considered how a PFR and a CMFR respond to an instantaneous pulse addition of tracer. Now, instead, consider how they respond to a *step change in the inlet concentration*. For time $t < 0$, the influent concentration is zero, i.e., the inlet is "clean". Then, at time $t = 0$, the influent concentration instantaneously changes to a constant value C_I. The chemical is non-reactive tracer.

   a. For a plug flow reactor, determine the effluent concentration $C_E(t)$. For the PFR, no calculations or derivations are necessary – you just have to think it through. Hint: what will be the effluent concentration for $t < \tau$? for $t > \tau$?

   b. For a CMFR, derive an equation for the effluent concentration $C_E(t)$. For this one, you'll have to use a mass balance. Think carefully about the "flow in" term and the initial condition. They are not the same as the pulse addition case. Solve the differential equation with the proper initial condition to get $C_E(t)$.

   c. Graph your functions from parts (a) and (b). Put both of them on the same graph. Graph the functions in normalized form, i.e., as C_E/C_I versus t/τ. Be sure to label your graph clearly so we can tell which one is which.

6. (20 pts) Consider a reactor that has a residence-time distribution (exit age distribution) function $E(t)$ given by the following graph.



a. What is the average residence time in the reactor? Hint: you can determine it mathematically (which would be a bit of a pain) or you can determine it by inspection.

b. Suppose a chemical entering this reactor undergoes first-order degradation with a rate coefficient $k_1 = 0.03\ \text{min}^{-1}$. Estimate/calculate the ratio C_E/C_I for this chemical assuming steady-state operation. What fractional conversion does this represent? Hint: use the segregated flow model. It's going to get messy. You might need to integrate by parts or look up an integral in an integral table.

c. Consider a PFR with the same τ and the same k_1 as this reactor. Estimate C_E/C_I for the PFR. What fractional conversion does this represent?

d. Consider a CMFR with the same τ and the same k_1 as this reactor. Estimate C_E/C_I for the CMFR. What fractional conversion does this represent?

e. Of the three reactors, which one is the most efficient? Which one is the least efficient? Which one is in the middle? Is this what you expected?

7. (20 pts) (This problem is based on one written by Prof Paul Roberts of Stanford University) Consider the same well-mixed reservoir as in problem (3). However, this time, instead of adding a slug of tracer at $t = 0$, we will rapidly add a 50-kg slug of a degradable chemical. The chemical degrades according to first-order kinetics with $k_1 = 0.001\ \text{min}^{-1}$.

a. Derive a formula for $C_E(t)$. Hint: use a mass balance!

problem 7 continues →

7. continued

b. Make a graph that shows $C_E(t)$ for the tracer (from problem 3) and for the degradable chemical (from part a of this problem). Label the curves clearly.

c. What fraction of the degradable chemical remains in the reactor when $t = 0.5\ \tau$? when $t = \tau$? when $t = 2\ \tau$?

d. The tracer leaves the reactor by only one mechanism – flowing out. But the degradable chemical leaves by two mechanisms – flowing out and degrading. For this problem, what fraction of the mass loss is due to flow, and what fraction of the mass loss is due to reaction? Hint: compare the relative magnitudes of the proper terms in your mass balance.

e. What is the average residence time of the degradable chemical in the reservoir? Hint: you can't just use $\tau = V/Q$. That is the average hydraulic residence time, but not the average residence time of the degradable chemical. You'll need to come up with some other way for determining the average residence time of the degradable chemical.

8. (20 pts) (This problem is based on one written by Prof Paul Roberts of Stanford University)

Consider a long section of an even longer channel. The section under consideration has a depth of 0.5 m, a width of 2.0 m, and a length of 5000 m. We will consider this channel section to be a plug-flow reactor. The flow rate $Q = 2.5\ m^3/min$, as in problems 4 and 6.

Suppose 50 kg of conservative tracer are added to the inlet of the channel. However, the mass is not added completely instantaneously. Instead, it is added over the 10-minute interval -5 min $< t <$ 5 min.

a. Estimate/calculate τ, the average hydraulic residence time in the channel.

b. Estimate/calculate C_0, the concentration of tracer in the "slug" after the pulse is added. Hint: the tracer mass of 50 kg is added into what volume of water over a 10-minute interval?

c. Graph the effluent concentration of the channel, $C_E(t)$, versus time. For comparison, on the same graph, include $C_E(t)$ for the CMFR from problem 4.

d. Discuss the graphs from part (c). In both cases, you had 50 kg of tracer added into a "reactor" of volume 5000 m^3. In both cases, the flow rate Q and the average hydraulic residence time τ are the same. Why, then, do the two graphs look so different?

e. Suppose that instead of tracer, we add a degradable chemical to the channel – the same degradable chemical as in problem (6). What fraction of the degradable chemical remains in the reactor when $t = 0.5\ \tau$? when t = τ? when $t = 2\ \tau$?

f. Compare your results from part (e) to the results from problem 6(c).

9. (20 pts) OK, there is not actually a problem 9 yet. I want to write a question that uses the tanks-in-series model to approximate the behavior of a real reactor. But I didn't have time to write a good problem yet. The next time I teach this class I will come up with a good tanks-in-series question.