

ENV 4417: WATER QUALITY & TREATMENT

Fall 2015
Problem set #4
Due Tuesday, Oct. 13

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For 2015, answer problem 1, then problem 3 or problem 4.

(Problem 3 is probably easier, but I am not sure – both should be challenging.)

1. (40 pts) Ozone (O_3) is a powerful disinfectant. A problem with ozone is that it decomposes relatively quickly in water; the effectiveness of ozone as a disinfectant depends partly on how fast it decomposes. Therefore, many researchers have investigated the kinetics of ozone decomposition in water. It is commonly (though not always) observed that the decomposition of ozone follows *second-order kinetics*. That is, the *rate* of ozone decomposition is given by $r = k_2 [O_3]^2$ where r is the reaction rate (mol/(L·s)), k_2 is a second-order rate constant, and $[O_3]$ is the molar concentration of ozone. At pH = 8 and T = 25 °C, k_2 is approximately 14 L/(mol·s).
 - a. Suppose the initial concentration of ozone in a *batch* reactor is 4 mg/L (a typical concentration for drinking water treatment). The water is at 25 °C and is buffered to remain at pH = 8. How long will it take until 99% of the ozone is gone? *Hint #1*: watch your units. *Hint #2*: You can look up second-order kinetics in a batch reactor...or derive the equation from a material balance!
 - b. Consider a case where ozone is added to water as it enters an ideal *plug-flow* reactor. The concentration of ozone in the influent water is 4 mg/L. The water is at 25 °C and is buffered to remain at pH = 8. The system is at steady state. The plug-flow reactor has a hydraulic residence time of 30 min. Will the ozone concentration remain above 1 mg/L throughout the reactor? Show your work to justify your answer. (We want to make sure that the ozone concentration in the water does not drop below 1 mg/L because it might not be a suitable disinfectant at concentrations below that level.) *Hint*: a PFR is like....
 - c. Now consider a case where ozone is added to water right before it enters an ideal *completely-mixed-flow* reactor (CMFR). The volumetric flow rate of the water is Q , the volume of the reactor is V , and the concentration of ozone in the influent water is C_1 . The system is at steady state. Write a *material balance* for ozone in the CMFR.
 - d. Re-arrange the terms in your material balance to derive an equation for the concentration of ozone exiting the CMFR. *Hint*: there are two possible solutions to your equation from part (c), but only one of them makes physical sense, so pick that one.
 - e. Suppose the average hydraulic residence time of a CMFR is 30 min and the influent ozone concentration is $C_1 = 4$ mg/L. The water is at 25 °C and is buffered to remain at pH = 8. The system is at steady state. What will be the concentration of ozone in the reactor effluent? *Hint*: use your answer from part (d).

2. (60 pts) This problem is based on material from the textbook *Water and Wastewater Engineering: Design Principles and Practice* [Davis, 2011]. Suppose that you are designing a disinfection process for a city drinking water plant. The design flow rate is 18,500 m³/d (about 5 mgd). You have selected ozone as your primary disinfectant. Your disinfection process must achieve 3 log inactivation of *Giardia*, 4 log inactivation of viruses, and 2 log inactivation of *Cryptosporidium*, in accordance with the Safe Drinking Water Act. Assume a water temperature of 5 °C.
- Look up the EPA's *Ct* tables to find out what *Ct* values are required to achieve the necessary log inactivations of the three pathogens with ozone. (I found the tables for *Giardia* and viruses on-line pretty easily. The table for *Cryptosporidium* is a bit tougher to find, but I did find it after just a few minutes of hunting.) Which pathogen will control the disinfection process?
 - From a bench-scale test, we determined that we can transfer 2.0 mg/L of ozone into the water when the pH is 7.0 and the temperature is 5 °C. What contact time is required? (Note that, under EPA guidelines, this contact time is t_{10} . This means that 10% of the contactor's residence-time distribution is lower than t_{10} -- which implies that 90% of the contactor's residence-time distribution is *greater* than t_{10} . Using t_{10} in the *Ct* calculation is intended to provide a measure of safety.)
 - A hydraulic analysis of the contactor's residence-time distribution found that $t_{10}/\theta = 0.65$ where θ is the average (mean) hydraulic residence time. Estimate the average hydraulic residence time.
 - It was observed that ozone decays according to second-order kinetics. The second-order rate constant is 3.5 L/(mol·s). Determine the rate constant if we change the units to L/(mg·min). The reason to do this is so that the rate constant has units consistent with your *Ct* values.
 - Suppose that your ozone contactor can be modeled as 10 well-mixed cells in series. For instance, perhaps it is an over-under baffled contactor with 10 chambers, and each one can be considered to be well-mixed. The ozone concentration entering the first cell is 2.0 mg/L based on the test mentioned above in part (b). What will be the concentration of ozone exiting the first cell? *Hint*: use a *material balance* to determine the equation for second-order reaction kinetics in a CMFR (...like what you did on problem 1). *Another hint*: you know the overall hydraulic residence time of the reactor, so you can easily estimate the hydraulic residence time in each cell. Assume steady-state operation of the ozone contactor.
 - Set up a spreadsheet in which you determine the concentration of ozone exiting each of the 10 cells. The effluent from cell #1 is the influent to cell #2, etc.
 - Calculate the *Ct* value in each of the cells in the ozone contactor. Assume that $t_{10}/\theta = 0.65$ in each cell and use t_{10} when you calculate *Ct*. Then determine the overall *Ct* value. Did you meet the *Ct* requirement that you found in part (a)?

problem 2 continues →

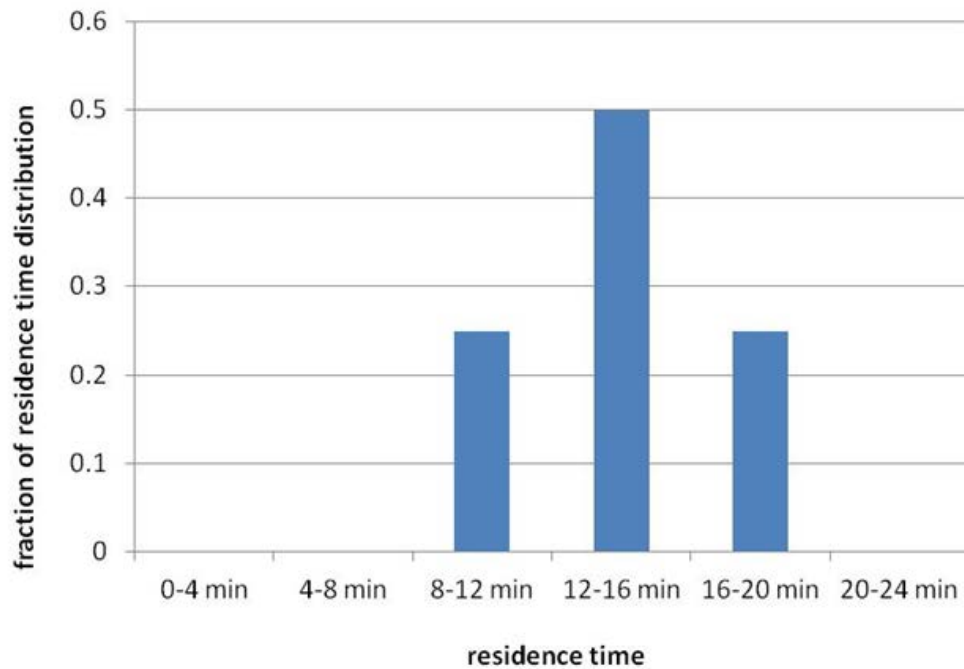
2. *continued*
- h. If your contactor doesn't meet the requirement, then you can either retrofit the contactor to make it bigger – a big hassle – or you can try to deliver a slightly higher dose of ozone. What influent dose of ozone would enable you to meet the Ct requirement? You can find this pretty easily by trial-and-error with your spreadsheet from part (f).
3. (60 pts) The city of Eau Claire has a problem at their drinking water plant. They can't meet their treatment objective of 99% disinfection of poliovirus. In this problem, you will help them figure out why not, and what they can do about it.
- Assume that 99% inactivation of poliovirus requires a Ct value of 150 if using chloramines and 15 if using free chlorine. Those values apply to a batch reactor or a plug-flow reactor. These are probably pretty good estimates.
 - The plant's operating flow rate is $2.43 \text{ mgd} = 383 \text{ m}^3/\text{hr}$.
 - The raw water at the plant contains 1.4 mg/L of ammonia nitrogen (i.e., 1.4 mg/L as N, not as NH_3).
 - The plant operators are dosing chlorine gas (Cl_2) at a rate of 60 kg/d .
- a. By convention, what are the units on the Ct values reported above?
- b. In a batch or plug-flow reactor, what value of kt is required to give 99% inactivation of pathogens? Here k is the apparent first-order rate coefficient (base e), and t is the contact time. You can assume that Chick's law holds, i.e., that inactivation follows first-order kinetics. Hint: you are finding the kt value that gives 99% inactivation in any batch or plug-flow reactor...it is not specific to the Eau Claire facility.
- c. Recall that the Chick-Watson model says that $k = \lambda C$, i.e., the first-order rate coefficient is linearly proportional to the dose of disinfectant. The parameter λ is called the "coefficient of specific lethality". Estimate λ for both free chlorine and combined chlorine. Hint: you know what kt is required for 99% inactivation (from part b), and you know what Ct is required for 99% inactivation.
- d. Based on the Cl_2 dose rate at the plant, what should be the concentration of chlorine residual in the disinfection contactor? Do you expect this to be free chlorine or combined chlorine? Explain briefly.
- e. Based on the concentration you found in part (d), what would be the value of the apparent (base e) first-order rate coefficient, k , for disinfection at the Eau Claire facility?

The engineers at Eau Claire were worried that maybe short-circuiting was causing their poor disinfection performance. They ran a tracer test on their chlorine contactor. They found a residence time distribution as shown in the figure on the next page.

problem 3 continues →

3. *continued*

Residence time distribution for use in part (f) and thereafter:



- f. Estimate the average hydraulic residence time and the volume of the contactor. Report your estimates in units of min and m^3 , respectively.
 - g. Estimate the percentage removal of poliovirus you would expect based on the current operation at Eau Claire. *Hint*: use all three parts of the residence-time distribution.
 - h. Compare the removal you found in part (g) to that which you would expect in a plug-flow reactor and in a completely-mixed flow reactor, each with the same value of k and the same average hydraulic residence time. Does Eau Claire's system behave more like a CMFR or more like a PFR?
 - i. What do you think is Eau Claire's major problem? i.e., why can't they meet the standard of 99% removal of poliovirus? What change would you recommend in order to improve the removal of poliovirus at the Eau Claire plant? Try to be quantitative with your recommendation.
4. (60 pts) *Adapted from a problem originally written by Prof Paul Roberts of Stanford University.* A water treatment plant is having difficulties meeting its coliform requirement (< 2 coliforms per 100 mL). They are treating a surface water supply with 10^3 coliforms per 100 mL. Ammonia is negligible. The volume of the chlorine contact tank is 1000 m^3 and the flow is $100 \text{ m}^3/\text{min}$. At the chlorine dose currently used (2 mg/L Cl_2), a residual of 1 mg/L is obtained. However, even with this chlorine residual, approximately 10 coliforms/100 mL remain in the effluent.

4. *continued*

- a. You are called in to determine the chlorine residual needed to assure less than 2 coliforms/100 mL in the finished water. You conduct a batch disinfection study at two dosage levels, with the following results:

	Experiment	
	A	B
Cl ₂ Dose (mg/L)	2	5
Cl ₂ Residual (mg/L)	1	3
	log₁₀(N₀/N)	
t = 1 min	0.5	1.0
t = 2 min	1.0	2.0
t = 5 min	2.5	5.0
t = 10 min	5.0	

Interpret the data using Chick's law and report the rate constants for cases A and B.

- b. The treatment plant manager doesn't believe your data. She tells you: "Your data from Experiment A show that I should have 5 log-kills after 10 minutes at a chlorine residual of 1 mg/L. I know I have a residual of 1 mg/L in my chlorine contactor, and my average hydraulic residence time is 10 min. Therefore, I should easily be achieving the effluent requirement at the present dosage. Your data must be wrong!" What other possible explanation can you suggest? How would you test its validity? (Hint: read parts c and d, below.)
- c. The manager throws you out of the office and begins to dose at 5 mg/L Cl₂, which yields a residual of 3 mg/L (as in Experiment B). Two months later, she calls you back. Even at the higher dose and the higher residual, she still finds coliforms in about half of the effluent samples. Furthermore, she is now receiving 50 complaints per week from customers regarding the taste and odor of the water. (...and I worry to think about the higher DBP formation, too!!) She now agrees with your suggestion in part (b) above, and conducts your proposed study. The results are shown in the table on the following page.
- d. What amount of tracer (mass) did you have to add (as a pulse) to get these results?
- e. What are the average hydraulic residence times of the unbaffled tank and the baffled tank? Based only on the average hydraulic residence time, which reactor (baffled or unbaffled) would you expect to offer better disinfection?

problem 4 continues →

4. *continued*

Time (min)	Tracer Concentration (mg/L)	
	Unbaffled Tank	Baffled Tank
1	0.02	0.01
3	0.1	0.03
5	0.16	0.06
7	0.16	0.12
9	0.13	0.28
11	0.1	0.28
13	0.064	0.12
15	0.048	0.06
17	0.036	0.03
19	0.03	0.01
25	0.016	0.005
35	0.01	
45	0.005	

- f. What effluent coliform concentration do you calculate for the unbaffled and baffled reactors based on the data in parts (a) and (c)? Calculate for both residual levels, 1 mg/L Cl₂ and 3 mg/L Cl₂. Do the calculated results for the unbaffled reactor agree with the plant manager's experience? What system would you recommend to meet the standard?
- g. Was your expectation from part (e) met? Why or why not? Comment briefly on the importance of residence-time distribution during disinfection.