ENV 6438: Physical and Chemical Processes for Treatment of Drinking Water
Department of Civil & Environmental Engineering
University of South Florida

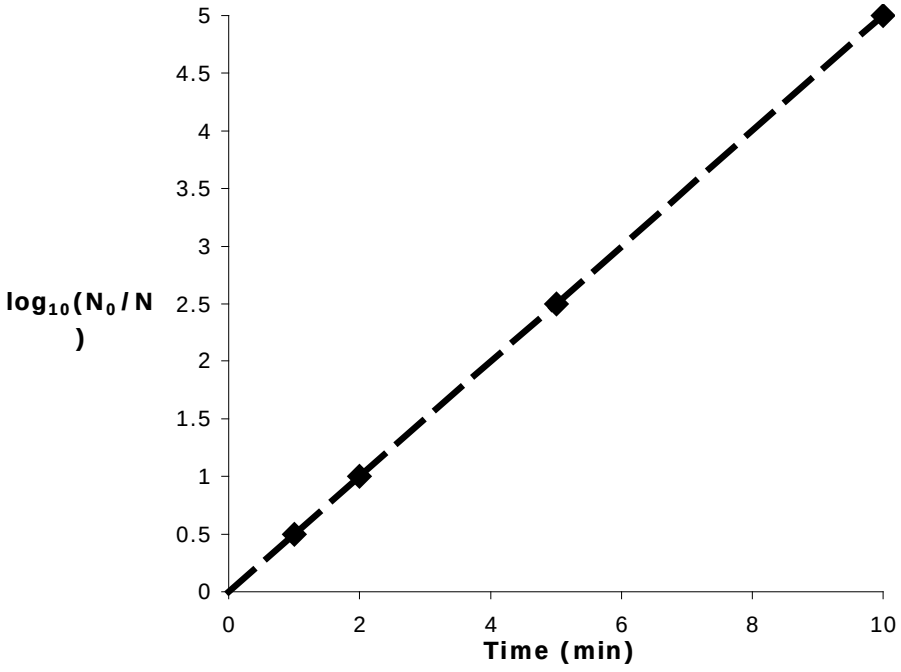
Cunningham **Spring 2020**

Homework #7 Topic: Disinfection Due Mon., April 13

Assignment for 2020: Answer problem 1; then choose *two* of problems 4, 5, 8.

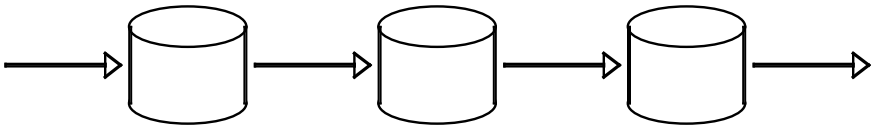
1. (20 pts)
   a. Answer question 13-4 in the Crittenden text (3rd edition).
   b. Answer question 13-5 in the Crittenden text (3rd edition).

2. Imagine that you are designing a chlorination system for a drinking water treatment plant. The design flow rate is 10 million gallons per day (1577 m^3/hr). You must provide a free chlorine residual of at least 1.0 mg/L chlorine in order to protect against contamination in the distribution system. However, you can not exceed a free residual of 2.0 mg/L chlorine, because you are worried about the formation of disinfection by-products. You are given the following data for disinfection of *Giardia lamblia*. The data were collected in a batch reactor, using a free residual C = 1.5 mg/L chlorine.



problem 2 continues →

2. continued
   a. From the graph, estimate the first-order rate constant k (in min^{-1}) for both base 10 and base e.
   b. Suppose your chlorine contactor is a well-stirred cylindrical tank. The diameter of the tank is 10 m and the depth (height) is also 10 m. What is the average hydraulic residence time, in units of minutes? If the contactor behaves as a CMFR, how much removal of *Giardia* would you get (i.e., what fractional removal)? Hint: be sure to use the proper rate constant k from part (a).
   c. Now suppose you had three smaller cylindrical tanks. The diameter of each tank is 7 m and the depth (height) of each is also 7 m. Each behaves as an ideal CMFR. You arrange the three tanks in series as shown below. Compare the average hydraulic residence time of the series configuration (i.e., for the water to pass through all three tanks) to the average hydraulic residence time of the larger tank from part (b).



series configuration

   d. Assuming the series configuration, what is the overall removal of *Giardia* that you will achieve?
   e. Look up the primary standard for disinfection of *Giardia* and report it. Do you meet the standard with one large tank (part b)? Do you meet the standard with three small tanks in series (part c)? Why?

3. Calculate the resultant pH if gaseous Cl_2 were added to "pure" water at an initial aqueous concentration of 10^{-4} M. Ignore the presence of carbonate and other ions not related to chlorination. Assume no reduced nitrogen is present. Hint: consider the hydrolysis of Cl_2 and the dissociation of HOCl. The species present should be H^+, OH^-, Cl_2 (aq), HOCl, OCl^-, and Cl^-. Therefore, you have six concentrations to calculate, and six equations: the hydronium-hydroxyl equilibrium, the hydrolysis of chlorine, the dissociation of hypochlorous acid, a mass balance for total chlorine, a second mass balance for chlorine based on stoichiometry, and charge neutrality.

4. (40 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 m^3/d. 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.
   a. 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?
   b. 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.)
   c. Suppose that the plant design engineer used this required value of t_{10} to design the full-scale disinfection reactor. The engineer estimated that $t_{10}/\tau = 0.65$ where τ is the average (mean) hydraulic residence time. What average hydraulic residence time will the reactor have?
   d. 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.
   e. Suppose that the ozone contactor consists of an initial contact chamber in which the ozone is delivered, followed by 10 well-mixed reactor cells in series. Ozone is delivered in the initial contact chamber but not in the 10 reactor chambers. The total residence time of the 10 reactor chambers is τ, which you found in part c. The ozone concentration going from the initial contact chamber into the first reaction chamber 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 for second-order reaction kinetics in a CMFR. 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.

problem 4 continues →

4. continued
   f. 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.
   g. Calculate the *Ct* value in each of the cells in the ozone contactor. Assume that $t_{10}/\tau = 0.65$ 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)? If not, why not? – after all, the reactor was designed based on the *Ct* value that you found – so it should meet the requirement, right? How could the reactor fail to meet the *Ct* criterion?
   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).

5. (40 pts) The city of Eauclaire has a problem at their drinking water plant. They can't meet their treatment objective of 99% disinfection of poliovirus. According to a figure in your text book, 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.

   - The plant's operating flow rate is 2.43 mgd = 383 m^3/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 Eauclaire 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.

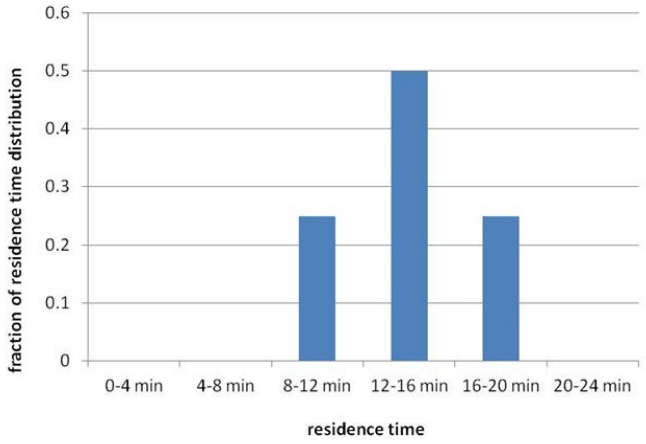
problem 5 continues →

5. continued
   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. Hint: Think about where you are on the "breakpoint chlorination" curve.
   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 Eauclaire facility?

   The engineers at Eauclaire 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 below.

   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 Eauclaire.
   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.
   i. What do you think is Eauclaire's major problem? What change would you recommend in order to improve the removal of poliovirus at the Eauclaire plant? If you can be quantitative with your recommendation, that would be great, but a qualitative answer is fine too.

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



The following problems are adapted from problems originally written by Prof Paul Roberts of Stanford University.

6. Chlorine is used for disinfection of a water containing negligible ammonia. Calculate the percent HOCl at pH 6, 7, 8, and 9 at 20˚C. If HOCl is a better disinfectant than OCl^- by a factor of 100, what is the relative germicidal effectiveness at these pH values (where pure HOCl would count as a value of 1.0)?

7. Treated wastewater (secondary effluent) containing 2.0 mg/L ammonia (as N) is to be disinfected with chlorine at pH 7.5.

Chlorine Dosage (mg Cl_2/L)	Chlorine Residual (mg/L as Cl_2)
3.0	2.0
6.0	4.0
8.0	5.4
11.0	7.2
14.0	3.2
16.0	2.0
18.0	2.4
20.0	4.4
24.0	8.0

   a. Estimate the free and combined residuals at dosages of 4.0 mg/L Cl_2 and 20.0 mg/L Cl_2.
   b. According to the data above, at what dosage does the breakpoint occur? If we assume NH_3 is destroyed according to the following reaction, at what chlorine dosage would the breakpoint theoretically occur?

$$3\ HOCl + 2\ NH_3 \rightarrow N_2 + 3\ H^+ + 3\ Cl^- + 3\ H_2O$$

   c. In what range of chlorine doses would you expect monochloramine to predominate?

8. (40 pts) 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 m^3/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, so the plant is not in compliance.

   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 results show in the table below (next page). Interpret the data using Chick's law; report the rate constants for cases A and B.

	Experiment	
	A	**B**
Cl_2 Dose (mg/L)	2	5
Cl_2 Residual (mg/L)	1	3
	$\log_{10}(N_0/N)$	
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	

   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 I know I have 10 minutes of residence time. Therefore, I should easily be achieving the effluent requirement at the present dosage. But I still have 10 coliforms per 100 mL. 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 Cl_2, which yields a residual of 3 mg/L (as in Experiment B). She figures that if a dose of 2 mg/L isn't working, surely a dose of 5 mg/L will work. But 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 agrees with your suggestion in part (b) above, and conducts your proposed study. The results are shown in the table on the next page. What amount of tracer (mass) did you have to add (as a pulse) to get these results?

problem 8 continues →

8. continued

	Tracer Concentration (mg/L)	
Time (min)	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	

d. Based on the data in parts (a) and (c), what effluent coliform concentration would you expect to see for the unbaffled and baffled reactors? Calculate for both residual levels, 1 mg/L Cl_2 and 3 mg/L Cl_2. Hint: use the general procedure shown in example 13-4 of your text book, but check if your kinetic data might allow a simpler analysis than the one from the text.

e. Do the calculated results for the unbaffled reactor agree with the plant manager's experience? What system would you recommend for this treatment plant?

f. Comment briefly on the importance of residence-time distribution during disinfection.

9. The equilibrium constant for the hydrolysis of Cl_2 to HOCl is 3.4×10^{-4} at 20 °C.

a. Compare the ratio of [HOCl] to [Cl_2] at pH 7 for freshwater with a chloride content of 50 mg/L, and for seawater with a chloride concentration of 10,000 mg/L. Would you expect aqueous Cl_2 to play a significant role during disinfection at typical operating conditions?

b. Under what circumstances would you expect a significant fraction of Cl_2 to remain unhydrolyzed?

10. a. Calculate the kill efficiency, expressed as $\log_{10}(N_0/N)$, for a completely mixed flow reactor assuming that the disinfection reaction is first-order with respect to the number concentration N of organisms. Assume a residence time of 10 minutes and a rate constant (base *e*) of 1.0/min. Calculate the kill efficiency in a plug flow reactor under the same conditions.
    b. How much residence time in the CMFR would be required to reach the same kill efficiency as in the plug flow reactor with a residence time of 10 minutes?

11. Name three <u>chemical</u> disinfectants that are most widely considered as alternatives to free chlorine. Compare their advantages and disadvantages relative to free chlorine.

12. You are designing chlorine gas storage facilities for a plant treating a flow of 0.1065 m^3/s. The water to be chlorinated contains 1.0 mg/L NH_3-N. Assume ideal breakpoint chlorination and that NH_3 is destroyed according to the following reaction:

    $$3\ HOCl + 2\ NH_3 \rightarrow N_2 + 3\ H^+ + 3\ Cl^- + 3\ H_2O$$

    Given that a free chlorine residual of 2.5 mg/L as Cl_2 is desired, calculate the amount of Cl_2 (in kg) needed daily.

13. Write a brief essay addressing the following questions. Write in 12-point font, 1.5 or double spacing, and do not exceed 1 page. (Shorter is OK as long as you answer all the questions asked.)
    What is the general disinfection goal for water treatment in the developing world? (e.g., are we trying to achieve a particular effluent standard? a certain number of pathogen log-kills? or is it more general than that?) To achieve this goal, what disinfection techniques might you consider in developing regions? What are the pros and cons of these different techniques? Does one technique appear "best" to you? Why or why not? For UV disinfection in particular, what are some of the difficulties of implementing this technique for village-scale disinfection?