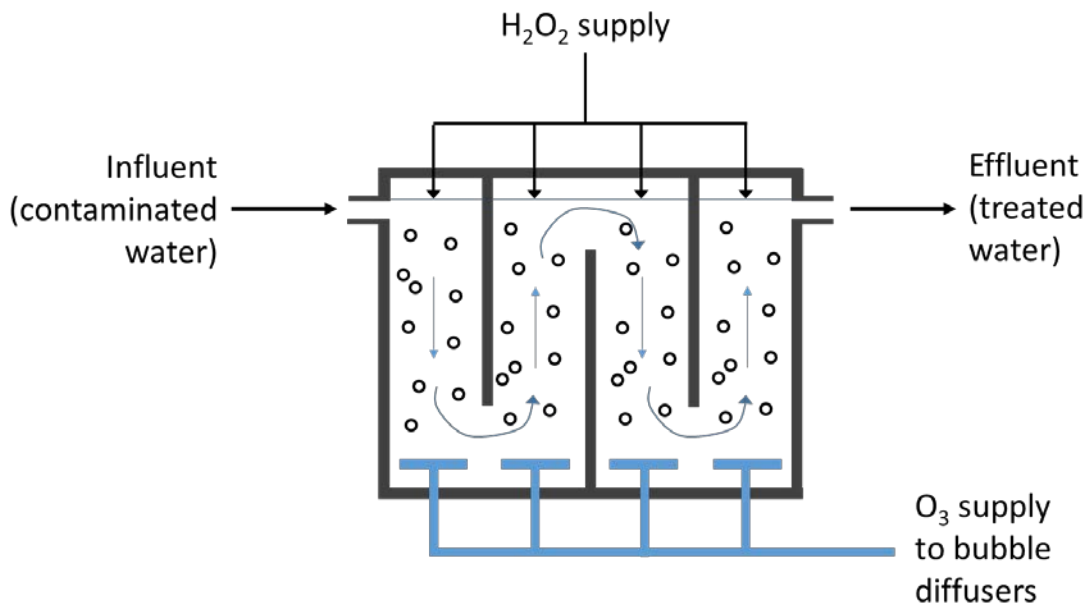


Spring 2021  
 Homework #8  
 Due Wed., March 16, 2021

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**HOMEWORK #8 HAS ARRIVED!**

Imagine that you want to treat a stream of contaminated groundwater with an advanced oxidation process (AOP). The volumetric flow rate of the contaminated water is 100 gpm, and it contains trichloroethene (TCE) at a concentration of 2.0 mg/L and 1,1,2-trichloroethane (TCA) at a concentration of 0.5 mg/L. You want to treat this contaminated groundwater via the addition of ozone ( $O_3$ ) and peroxide ( $H_2O_2$ ) to generate hydroxyl radicals ( $\cdot OH$ ). This process is best accomplished in a plug flow reactor. You will use the reactor configuration shown in the figure below; this is a typical reactor configuration for ozonation, and it could be applied relatively easily for the  $O_3/H_2O_2$  advanced oxidation process by dosing in some peroxide (as shown in the figure). From the figure, you can see that the water flows sequentially through four chambers in the reactor; you may treat each of the four chambers as a completely mixed flow reactor. (Note 1: You may know from previous classes that a series of completely mixed flow reactors behaves approximately like a plug flow reactor.) (Note 2: In reality, the assumption of complete mixing in each of the four chambers is somewhat questionable, because these reactors are susceptible to channeling; but for this assignment, treat each chamber as completely mixed – it is a decent model.)



Here is some additional information about the process:

- The total reactor volume is  $20 \text{ m}^3$ , i.e., each chamber is  $5 \text{ m}^3$ .
- The temperature of the contaminated water is  $15 \text{ }^\circ\text{C}$ . You may assume that reaction rate coefficients measured at  $25 \text{ }^\circ\text{C}$  are valid even at this lower temperature. (They probably aren't, but let's make the assumption anyway...it's OK for the purposes of this exercise.)
- Ozone is introduced into the reactor through fine-bubble diffusers in the bottom of each chamber of the reactor. The design rate of ozone addition is 12 pounds (mass) of ozone per day to *each* chamber. (Note: this is a design rate; it might not be the actual rate of  $\text{O}_3$  delivery, but it helps us calculate the rate of  $\text{H}_2\text{O}_2$  dosing.) The partial pressure of ozone in the inlet gas is 0.07 atm. The overall mass-transfer rate coefficient for ozone dissolution into the water is  $K_{La} = 3 \times 10^{-4} \text{ s}^{-1}$ . Henry's constant for ozone is 83.9 atm•L/mol at  $23 \text{ }^\circ\text{C}$ ; you should look up or estimate the proper value for  $15 \text{ }^\circ\text{C}$ .
- Peroxide is dosed into each chamber of the reactor to react with the ozone and generate hydroxyl radicals. The design rate for peroxide addition is 0.5 pounds of peroxide per pound of ozone. Therefore, we dose 6 pounds of peroxide per day to *each* chamber.
- The groundwater has a pH of 7.0. It contains 210 mg/L of bicarbonate ( $\text{HCO}_3^-$ , as bicarbonate, not as  $\text{CaCO}_3$ ) and 1.2 mg/L of dissolved organic carbon (DOC).

Based on this design and this information, answer the following questions. ***I strongly recommend that you set up a spreadsheet to perform your calculations. It will make your life much easier when you get to problems 2 and 3.***

1. (35 pts)

- a. Calculate the average hydraulic residence time in each chamber of the reactor. Report your answer in both minutes and seconds.
- b. Calculate the *influent* concentration, in mol/L, of the following chemical species: TCE, TCA,  $\text{HCO}_3^-$ , DOC,  $\text{H}_2\text{O}_2$ ,  $\text{HO}_2^-$ . Argue or demonstrate that it is not important to consider the presence of carbonate,  $\text{CO}_3^{2-}$ . For the influent concentration of  $\text{H}_2\text{O}_2$  and  $\text{HO}_2^-$ , consider only the first chamber of the reactor – these chemicals are added to all four chambers, but for now consider only the first chamber.
- c. Use equation 18-49 from your text book to estimate the concentration of hydroxyl radicals,  $[\cdot\text{OH}]$ , in the first chamber of the reactor at steady state. Be sure to account for both the TCE and the TCA. Report the concentration in mol/L. Note that this estimate is based on the *influent* concentrations of each of the chemical species, and therefore it probably underpredicts  $[\cdot\text{OH}]$ . (...though there some other assumptions built in, too, so it *could* actually overpredict  $[\cdot\text{OH}]$ ...but most likely, equation 18-49 gives an underprediction of  $[\cdot\text{OH}]$ .)

problem 1 continues →

1. continued

- d. Based on the estimated [ $\cdot\text{OH}$ ] from part (c), estimate the *effluent* concentration of TCE, TCA, DOC, and  $\text{HCO}_3^-$  from the first chamber of the reactor (i.e., flowing from the first chamber to the second). Report your answers in mol/L and in mg/L. Hint: for a first-order reaction in a completely mixed flow reactor (CMFR) at steady state, we know

$$C_E = C_I \frac{1}{1 + k_1 \tau}$$

where  $\tau$  is the average hydraulic residence time of the reactor. (Think about how you will estimate  $k_1$  for each of the relevant chemicals. Each chemical will have its own value of  $k_1$ .)

- e. Estimate the concentration of ozone,  $\text{O}_3$ , in the first chamber of the reactor. Use equation 18-50 and the procedure shown in example 18-6 of your text book. For now, you still have to use the *influent* concentrations of  $\text{H}_2\text{O}_2$  and  $\text{HO}_2^-$  to do your calculations. We would rather use the concentrations of  $\text{H}_2\text{O}_2$  and  $\text{HO}_2^-$  that are *in* the reactor, but we don't know those concentrations quite yet. For now, you can use the text book's version of 18-50; later, we'll need the modified version that we derived in class.
- f. Now you can estimate the concentration of peroxide,  $\text{H}_2\text{O}_2$ , *in* the first chamber of the reactor. Use the procedure given in example 18-6 of your text book. Then, assuming that the pH is 7.0 in the first chamber of the reactor, estimate the concentration of  $\text{HO}_2^-$  in that chamber. Hint: use the pKa for  $\text{H}_2\text{O}_2$  dissociation.
- g. You now have estimates of the concentrations of all important chemical species in the first chamber of the reactor! (Recall that, for a CMFR, the concentration of a chemical species *in* the reactor is equal to the concentration *exiting* the reactor.) Using this information along with equation 18-48, re-calculate the concentration of the hydroxyl radical, [ $\cdot\text{OH}$ ], in the first chamber of the reactor. For now, you can use the text book's version of 18-48; later, we'll need the modified version that we derived in class. Include both terms in the numerator, i.e., do not neglect the ozone concentration in the numerator. How much did your estimate of [ $\cdot\text{OH}$ ] change between part c and part g?

Now here is where the fun really begins!!! We can *iterate* parts (d)–(g) of problem 1 until we determine the correct hydroxyl radical concentration and the correct effluent concentrations of each chemical species in the first chamber. This is a little tricky but I will lead you through it. If you have set up a spreadsheet to handle your calculations, it isn't too difficult as long as you follow the directions below. If you try to do it by hand, then you have quite a few late nights ahead of you. Here is how to proceed:

- i. Make an initial guess at the concentrations of hydroxyl radicals and peroxide in the first chamber of the reactor. You can use the outputs from problem 1(f) and 1(g) as your initial guess.
- ii. Calculate  $[\text{HO}_2^-]$  from your guess of  $[\text{H}_2\text{O}_2]$ . Assume  $\text{pH} = 7$  in the reactor.
- iii. Estimate apparent first-order rate constants for the disappearance of TCE, TCA, bicarbonate, and NOM (or DOC). From the first-order rate constants and the known *influent* concentrations of the chemical species, estimate the *effluent* concentrations of TCE, TCA, bicarbonate, and DOC from the first chamber of the reactor.
- iv. Estimate the concentration of ozone,  $[\text{O}_3]$ , in the first chamber of the reactor vessel. Use the *modified* form of equation 18-50 which I gave in class.
- v. Estimate  $k_{\text{H}_2\text{O}_2}$ , the apparent first-order rate constant for the disappearance of  $\text{H}_2\text{O}_2$ . I gave the equation in class.
- vi. Estimate the effluent concentration of  $\text{H}_2\text{O}_2$  from the first chamber of the reactor. Use the rate constant from step v.
- vii. Estimate  $[\text{HO}_2^-]$  from the effluent  $[\text{H}_2\text{O}_2]$ .
- viii. From the estimated effluent concentrations, calculate the denominator of equation 18-48.
- ix. Use our *modified* version of equation 18-48 (from class) to get a new, updated estimate of the hydroxyl radical concentration,  $[\cdot\text{OH}]$ , in the first chamber of the reactor. Use all the terms in the numerator, i.e., do not assume any terms are negligible.
- x. You now have updated estimates of  $[\cdot\text{OH}]$ ,  $[\text{H}_2\text{O}_2]$ , and  $[\text{O}_3]$ . Compare these to the guesses that you made back in step i, and/or the values from problem 1. If they are the same, then you are done. If they are not the same, then you need to make a new guess and repeat steps ii–x again. Continue until it converges!

Once your solution converges, answer the following questions.

2. (30 pts)

- a. What is the concentration of hydroxyl radicals in the first chamber of the reactor? How does this compare to your estimates from problem 1?
- b. What fractional removal of TCE and TCA did you achieve in the first chamber of the reactor? Did you meet the treatment objectives of  $5 \mu\text{g/L}$  for each compound in the first chamber? [That is the drinking water MCL for each chemical.] How close did you come to meeting the treatment objective? Which chemical is removed more effectively, TCE or TCA? Why?
- c. Your book says that it is probably OK to ignore the aqueous concentration of ozone in the numerator of 18-48. Do you find that to be true, or do you think it is important to include it in your calculations?

problem 2 continues →

2. continued

d. What appears to be the major impediment to the success of the AOP? Hint: what chemical species is responsible for keeping  $[\cdot\text{OH}]$  low? Based on that, how might you modify this AOP process to make it more successful?

3. (25 pts) In problems 1 and 2, we considered only the first chamber of the reactor. Now let's consider the entire reactor, i.e., all four chambers. The effluent stream from the first chamber becomes the influent stream to the second chamber, the effluent from the second chamber becomes the influent to the third chamber, etc. Each chamber receives ozone at 12 lb/day and is also dosed with peroxide at a rate of 0.5 pounds peroxide per pound of ozone. Determine the concentrations of TCE, TCA,  $\text{H}_2\text{O}_2$ , DOC, and  $\text{HCO}_3^-$  in the effluent of chambers 2, 3, and 4. This sounds awful, but it is actually not too difficult. Here is what I recommend.

- Copy your spreadsheet from problems 1 and 2.
- Adjust the influent concentrations as needed. For TCE, TCA, bicarbonate, and NOM, the concentration flowing *into* the second chamber will be the concentration flowing *out of* the first chamber, the concentration flowing *into* the third chamber will be the concentration flowing *out of* the second chamber, etc.
- For peroxide, you should account for the concentration that flows from one chamber to the next, *plus* the dose added to each chamber.
- The *modified* versions of equations 18-48 and 18-50 (which you used in problem 2) account for the fact that ozone is flowing in and out of the chambers. The equations in the text assume that no ozone flows in, and that the ozone flowing out is negligible; these might not be good assumptions, so we use the modified versions to account for ozone entering and exiting the chambers.

Examine your final effluent concentrations. Does the final effluent of the reactor meet the treatment objective for TCE and TCA? If not, how many additional chambers do you think your reactor would need?

4. (10 pts) In problems 1–3, you considered the destruction of TCE and TCA. In your design project this semester, you must also remove cis-1,2-dichloroethene (cis-DCE) and 1,1,2,2-tetrachloroethane (TeCA) from the contaminated water. The second-order rate constants for the reactions of cis-DCE and 1,1,2,2-TeCA with the hydroxyl radical are *not* given in your text book.

Problem 4 continues →

4. continued

- a. Estimate the values of these rate constants. Here is what I recommend: tabulate the values of the second-order rate constants,  $k_R$ , for all *chlorinated ethenes* and *chlorinated ethanes* that you can find in your text book. Use Table 18-2 and, if you can access it, Table E-4 (see footnote of Table 18-2). Look for patterns as to how  $k_R$  changes with increasing number of chlorine atoms, for ethenes versus ethanes, etc. Then, based on these patterns and measured values for similar contaminants, decide what you think might be reasonable values for  $k_R$  of cis-DCE and 1,1,2,2-TeCA. You can use these values later this semester in your design project. Try to make your estimates sufficiently conservative such that you do not under-design your AOP in the design project.
- b. Compare your estimate of the rate constant for 1,1,2,2-TeCA to the value reported by Chen et al. (2006) in their Table 2. Do you wish to modify your estimate, or do you think your estimate from part (a) is good enough to use for your design project?

Note: On problem 4, I don't actually know what the "right" answer is. You must learn how to make reasonable estimates which you can then use in engineering design calculations. Making good estimates and good judgements is an important part of engineering design. A lot of the homework questions this semester have tried to get you to think about things like: "How would I actually do this in practice? If my boss came to me and gave me this design problem, what would I do? What is a reasonable approach that I would feel comfortable presenting to a potential client?" These types of decisions are just as important as being able to perform the calculations which ensue.

5. NOT GRADED – JUST FOR FUN

Make a copy of your spreadsheet from problems 1–3. Adjust the ozone mass transfer rate coefficient,  $K_L a$ , up by a factor of 10. What happens? Does it affect how many chambers are needed to meet the treatment objective? Now adjust the ozone mass transfer rate coefficient down by a factor of 10 from its default value. Now how effective is the system? What do you conclude about the sensitivity of the system performance to the value of  $K_L a$ ?

6. NOT GRADED – JUST FOR FUN

Make a copy of your spreadsheet from problems 1–3. Adjust the peroxide addition rate. Instead of 0.5 lb H<sub>2</sub>O<sub>2</sub> per lb O<sub>3</sub>, try peroxide addition rates of 0.25 lb/lb and 1.0 lb/lb. What happens? Does it affect how many chambers are needed to meet the treatment objective? What do you conclude about the sensitivity of the system performance to the peroxide addition rate?

(...We could also examine the effect of the DOC concentration, the HCO<sub>3</sub><sup>-</sup> concentration, etc.)