

ENV 6519: Physical and Chemical Processes in Environmental Engineering

Spring 2009

**Examination**

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University of South Florida

Civil & Environmental Eng.

J. A. Cunningham

**Instructions:**

1. You may read these instructions, but do not turn the page or begin working until instructed.
2. Answer all questions in the exam booklet provided, and write your name conspicuously on the exam booklet. (APEX students taking the exam off-site should provide their own paper.)
3. You are allowed one sheet of 8.5-by-11-inch paper (or A4 paper) with hand-written notes. You may write on both sides of that paper. However, mechanical reproductions (photocopying, laser printing, scanning, etc.) are not allowed; all notes must be hand-written.
4. A calculator is recommended, but it may not be pre-programmed with formulae from the class.
5. Time limit: 70 minutes. Stop working when asked. If you continue working after time has been called, you will be penalized at a rate of 1 point per minute.
6. Show all work and state all assumptions in order to receive maximum credit for your work.
7. Make sure your answers include units if appropriate. Watch your units!!!!
8. This exam contains 3 questions, all with multiple parts. ***Choose any two of the three problems.*** If you attempt all three, you will be given credit for the two on which you score highest. However, this is probably not a good strategy; you are probably better off concentrating on two problems and trying to do them well, rather than attempting all three.
9. The total point value for the exam is 70 points -- one point per minute. Gauge your time accordingly!
10. Use a reasonable number of significant digits when reporting your answers. *You are likely to be graded down* if you report an excessive number of significant digits. In some cases, the problem may indicate the precision to which you should report your answer.
11. Don't cheat. Cheating will result in appropriate disciplinary action according to university policy. More importantly, cheating indicates a lack of personal integrity.
12. Page 2 of this exam (the back of this page) contains background information, data, constants, and conversion factors that might be helpful to you as you complete the exam. I recommend that you read page 2 carefully, as it is likely that you will need some of that information to complete the problems on the exam.
13. Additional pages, photocopied from your course text, are provided to give you additional information. You might or might not find the information useful.

## Background Information

Chloroform,  $\text{CHCl}_3$ , is a common water contaminant. It is also called trichloromethane. Chloroform is created inadvertently when water is disinfected with chlorine. It is also present in a significant number of contaminated groundwater sites because chloroform can be used as a solvent or an industrial chemical.

In this exam, we will consider the possible removal of chloroform from water by the three physical/chemical processes we have looked at during the semester. The concentration of chloroform in our contaminated water is  $100 \mu\text{g/L}$ , and we need to reduce it down to  $50 \mu\text{g/L}$  or lower. This doesn't sound too challenging -- only 50% removal required -- but let's see how it turns out.

### Properties of chloroform at 25 °C:

Molecular weight:	119.38 g/mole
Liquid density:	$1.48 \text{ g/cm}^3 = 1480 \text{ kg/m}^3$
Vapor pressure, $P^{\text{sat}}$ :	25,000 Pa
Aqueous solubility:	$0.071 \text{ mol/L} = 8.5 \text{ g/L}$
Octanol-water partition coefficient:	$10^{1.95} = 89$
Reaction rate constant with $\cdot\text{OH}$ :	$5.0 \times 10^6 \text{ L}/(\text{mole}\cdot\text{sec})$
Heat of vaporization, $\Delta H$ :	$8.80 \text{ kcal/mole} = 36.8 \text{ kJ/mole} = 36,800 \text{ J/mole}$

### Potentially useful constants:

Ideal gas constant, R:	$8.314 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 82.06 \times 10^{-6} \text{ atm}\cdot\text{m}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
Molecular weight of water, $\text{H}_2\text{O}$ :	18.01 g/mole
Density of water at 25 °C:	0.9970 g/mL
Viscosity of water at 25 °C:	$0.890 \times 10^{-3} \text{ Pa}\cdot\text{sec}$
Density of air at 25 °C:	$1.18 \text{ kg/m}^3$
Viscosity of air at 25 °C:	$1.85 \times 10^{-5} \text{ Pa}\cdot\text{sec}$

### Potentially useful conversion factors:

Pressure:	$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr} = 101325 \text{ Pa}$
Mass:	$1 \text{ kg} = 1000 \text{ g} = 10^6 \text{ mg} = 10^9 \mu\text{g}$
Temperature:	$25 \text{ }^\circ\text{C} = 298.15 \text{ K}$
Volume:	$1 \text{ m}^3 = 1000 \text{ L} = 10^6 \text{ mL} = 10^6 \text{ cm}^3$
Other :	$1 \text{ Pa} = 1 \text{ N/m}^2 = 1 \text{ kg}/(\text{m}\cdot\text{sec}^2)$

### Atomic Masses:

H = 1.008 g/mole    C = 12.011 g/mole    N = 14.007 g/mole    O = 15.999 g/mole

1. (35 pts) Imagine that you are investigating whether *adsorption onto activated carbon* is a good treatment technique for the removal of chloroform from water.

To conduct your investigation, you set up two laboratory-scale beds of granular activated carbon (GAC). Each contactor is 12.0 cm long and has a diameter of 6.0 cm. (Each one is about the size and shape of a 12-ounce soda can.) Through each contactor, you pump  $17 \text{ cm}^3/\text{min}$  of water that contains chloroform. In the first contactor, the influent concentration of chloroform is  $1000 \text{ }\mu\text{g/L}$ . In the second contactor, the influent concentration of chloroform is  $200 \text{ }\mu\text{g/L}$ .

Both contactors exhibited very sharp breakthrough curves, i.e.,  $t_{br} \approx t_m$  and  $\theta_{br} \approx \theta_m$ . This indicates a narrow mass-transfer zone as the contaminant moves through the carbon beds. In the first contactor, breakthrough occurred after  $\theta_m = 2,650$  bed volumes were treated. In the second contactor, breakthrough occurred after  $\theta_m = 5,340$  bed volumes were treated.

Each pilot-scale GAC contactor has the following characteristics.

carbon type = Calgon Filtrasorb F-400

bed length,  $L = 12.0 \text{ cm}$

bed diameter =  $6.0 \text{ cm}$

GAC grain diameter,  $d_p = 0.2 \text{ mm}$

GAC grain internal porosity,  $\varepsilon_p = 0.67$

Intergranular porosity of bed,  $\varepsilon = 0.4$

Bulk density of carbon in the bed,  $\rho_f = 480 \text{ kg/m}^3$

- a. (6 pts) Explain why  $\theta_m$  is different in the two contactors. Hint: the adsorption of chloroform onto this carbon exhibits a *favorable isotherm*.
- b. (5 pts) Based on the given breakthrough information, estimate/calculate the carbon *usage rate* for each of the two contactors.
- c. (8 pts) Assume that the adsorption of chloroform onto this carbon can be described well with a Freundlich isotherm. Demonstrate that  $1/n = 0.5647$ . Hint: use the *ratio* of  $\theta_m$  values for the two contactors.
- d. (6 pts) Find the Freundlich isotherm parameter  $K_F$ . Report the value in units of  $(\mu\text{g/g})/(\mu\text{g/L})^{1/n}$ . Hint: use one of the given values of  $\theta_m$  along with the value of  $1/n$  given in part (c).
- e. (6 pts) Suppose that the treatment process is economical only if we are able to treat at least 10,000 bed volumes before breakthrough. What range of influent concentrations would make this possible?
- f. (4 pts) Suppose that we have a contaminated water with  $100 \text{ }\mu\text{g/L}$  of chloroform, and we need to treat it down to  $50 \text{ }\mu\text{g/L}$  or lower. Would this GAC be a good engineering choice? Explain why or why not.

2. (35 pts) Imagine that you are investigating whether *air stripping* is a good treatment technique for the removal of chloroform from water.

You will use packed-tower aeration to treat the contaminated water. The incoming chloroform concentration is 100  $\mu\text{g/L}$ . The effluent concentration must be no greater than 50  $\mu\text{g/L}$ , i.e., you need to achieve at least 50% removal of the chloroform in the tower.

The air stripping tower has the following parameters.

Tower diameter = 1.0 m	Packing factor, $C_f = 20$
Packing type = 2" plastic saddles	Packing specific surface area, $a_t = 110 \text{ m}^2/\text{m}^3$
Packing diameter, $d_p = 0.0508 \text{ m}$	Packing surface tension, $\sigma_c = 0.033 \text{ N/m}$

Volumetric flow rate of water,  $Q = 200 \text{ gpm} = 0.0126 \text{ m}^3/\text{s}$

Overall inter-phase mass transfer rate constant for chloroform,  $K_L a = 0.0052 \text{ sec}^{-1}$

- (5 pts) Estimate/calculate Henry's constant,  $H$ , for chloroform at a temperature of 25  $^\circ\text{C}$ . Report  $H$  in its dimensionless form. Hint: watch your units!!
- (5 pts) Suppose we want to operate at a stripping factor  $S = 2.0$ . What air flow rate ( $Q_a$ ) is required? Report your answer in  $\text{m}^3/\text{s}$ .
- (5 pts) Based on these values of  $Q_a$  and  $S$ , estimate/calculate the concentration of chloroform that will be in the air stream exiting the top of the tower. Report it in units of  $\mu\text{g/L}$ .
- (6 pts) On the piece of graph paper provided, make a graph of the *equilibrium line* and the *operating line* for this air-stripping operation. Indicate on the graph the points that correspond to the top of the tower and the bottom of the tower. Be sure to put your name on the graph and turn it in with your exam booklet.
- (4 pts) Estimate the *height of a transfer unit*, HTU, under these conditions.
- (10 pts) Do you think the air stripping process looks like a good engineering option to achieve 50% removal of the chloroform in the water? Explain why or why not. Include other calculations or demonstrations that you think are necessary to support your answer. You have about 10 minutes to answer this question, so you will not be able to consider every aspect of the process in great detail. Try to consider the factors that you think are most important and that can be reasonably addressed in about 10 minutes.

3. (35 pts) Imagine that you are investigating whether *oxidation by ozone with hydrogen peroxide* is a good treatment technique for the removal of chloroform from water.

You will build a completely-mixed flow reactor (CMFR) through which the contaminated water flows. Ozone is bubbled into the bottom of the reactor, and hydrogen peroxide is added to the contaminated water just before it enters the reactor. This enhances the formation of the  $\cdot\text{OH}$  radical to destroy the chloroform. The average hydraulic residence time in the reactor is  $\tau = 6.0$  min (a pretty realistic value). The temperature of the system is  $25^\circ\text{C}$ .

The incoming chloroform concentration is  $100\ \mu\text{g/L}$ . The effluent concentration must be no greater than  $50\ \mu\text{g/L}$ , i.e., you need to achieve at least 50% removal of the chloroform in the reactor.

- a. (5 pts) Find the value of the apparent first-order rate constant,  $k$ , that will enable you to achieve your treatment objective in this reactor. Hint: recall that, for a CMFR,

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

- b. (6 pts) Find the hydroxyl radical concentration,  $[\cdot\text{OH}]$ , that must be present in the reactor to provide the necessary value of  $k$ .
- c. (6 pts) Suppose that the concentration of  $\cdot\text{OH}$  radical in the reactor is approximately given by

$$[\cdot\text{OH}] = \frac{(7 \times 10^{-4} \text{ sec}^{-1})(8.3 \times 10^{-4} \text{ mole/L})}{k_{\text{HCO}_3}[\text{HCO}_3^-] + k_{\text{R}}[\text{CHCl}_3]}$$

where  $k_{\text{HCO}_3} = 8.5 \times 10^6 \text{ L}/(\text{mole}\cdot\text{sec})$ ,  $[\text{HCO}_3^-]$  indicates the molar concentration of bicarbonate in the reactor, and  $[\text{CHCl}_3]$  indicates the molar concentration of chloroform in the reactor. Based on this, what is the maximum concentration of bicarbonate that can be present in the reactor if we want to meet our treatment objective?

- d. (8 pts) Based on your answer to part (c), what is the maximum *influent* concentration of bicarbonate that can be present in the contaminated water?
- e. (5 pts) The formula given in part (c), above, does not account for the presence of natural organic matter (NOM; also called dissolved organic carbon, DOC) in the water. If we accounted for the presence of NOM, how would the equation in part (c) change? Write down the new equation. Would this lead to a *higher* or *lower* allowable concentration of bicarbonate? Explain briefly.
- f. (5 pts) Do you think the ozone/peroxide process looks like a good engineering option to achieve 50% removal of the chloroform in the water? Explain why or why not.

Name: \_\_\_\_\_

