ENV 6519: Physical and Chemical Processes for Groundwater Remediation

Spring 2021 University of South Florida
Examination Civil & Environmental Eng.
Tuesday, March 30, 2021 J. A. Cunningham

Instructions:

1. You may read these instructions, but do not turn the page or begin working until instructed.
2. If an exam booklet (e.g., a "blue book") is provided, answer all questions in the exam booklet provided, and write your name conspicuously on the exam booklet. If no booklet is provided, use your own paper, write your name on each page, and staple them together before submitting.
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. ***Answer any two***.
9. If you attempt all 3 questions, make it clear which two you want me to grade. Otherwise, I will select the two which I think I can grade the fastest; this is not likely to work to your advantage.
10. The total point value for the exam is 100 points. Gauge your time accordingly!
11. 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.
12. Don't cheat. Cheating will result in appropriate disciplinary action according to university policy. More importantly, cheating indicates a lack of personal integrity.
13. Page 2 of this exam contain background information, data, constants, and conversion factors that might be helpful to you as you complete the exam. Read the background information carefully.
14. Additional pages, some photocopied from your course text, are provided to give you additional information (pp 3–5 of this exam). You might or might not find the information useful.
15. Hint #1: When you are working on these problems, answer each part of the question *in order*. That is, answer part (a) before you do part (b); answer part (b) before you do part (c); etc. You may need the answers from the earlier parts in order to answer the later parts.
16. Hint #2: If you don't know how to do one of the parts of the problem, just write "I do not know how to do this, so I will assume an answer of _____," and then pick a *reasonable* value. That will enable you to move on and answer the later parts of the question.

Background Information

The chemical 1,2-dibromoethane is also commonly called “ethylene dibromide” (EDB). The name EDB isn’t actually chemically accurate, but it is the name that many people use in practice anyway. EDB is a soil fumigant, formerly used a lot in strawberry production which is a big deal here in Florida. Use of EDB has been discontinued because EDB causes a variety of health effects. However, many sites remain where the soil and/or groundwater are contaminated with EDB. In this exam, we will consider the possible removal of EDB from water by the three physical/chemical processes that we have studied during the semester.

Properties of EDB at 25 °C:

Molecular formula	$C_2H_4Br_2$
Molar mass	187.86 g/mol
Liquid density	2.18 g/cm^3 = 2180 kg/m^3
Vapor pressure, P^{sat}	1620 Pa
Aqueous solubility, C^{SL}	0.0234 mol/L = 4.40 g/L
Octanol-water partition coefficient	$10^{1.96} = 91$
Reaction rate coefficient with $^{\bullet}$OH (L/(mol•s))	not given by your text book
Heat of vaporization, ΔH_{vap} (kJ/mol)	not given by your text book

Potentially useful constants:

Ideal gas constant, R: 8.314 Pa•m^3•mol^{-1}•K^{-1} = 82.06×10^{-6} atm•m^3•mol^{-1}•K^{-1}
Gravitational acceleration, g: 9.81 m/s^2
Molecular weight of water, H_2O: 18.01 g/mol
Density of water at 25 °C: 0.997 g/mL = 997 kg/m^3
Viscosity of water at 25 °C: 0.89×10^{-3} Pa•s = 0.89×10^{-3} kg/(m•s)
Density of air at 25 °C: 1.18 kg/m^3
Viscosity of air at 25 °C: 1.85×10^{-5} Pa•s = 1.85×10^{-5} kg/(m•s)

Atomic Masses:

H = 1.008 g/mol C = 12.011 g/mol N = 14.007 g/mol O = 15.999 g/mol
Cl = 35.453 g/mol Br = 79.904 g/mol

Potentially useful conversion factors:

Pressure: 1 atm = 760 mm Hg = 760 torr = 101325 Pa
Mass: 1 kg = 1000 g = 10^6 mg = 10^9 μg
Temperature: 25 °C = 298.15 K
Volume: 1 m^3 = 1000 L = 10^6 mL = 10^6 cm^3
1 gal = 3.785 L
Other: 1 Pa = 1 N/m^2 = 1 kg/(m•s^2)
1 J = 1 N•m = 1 kg•m^2/s^2

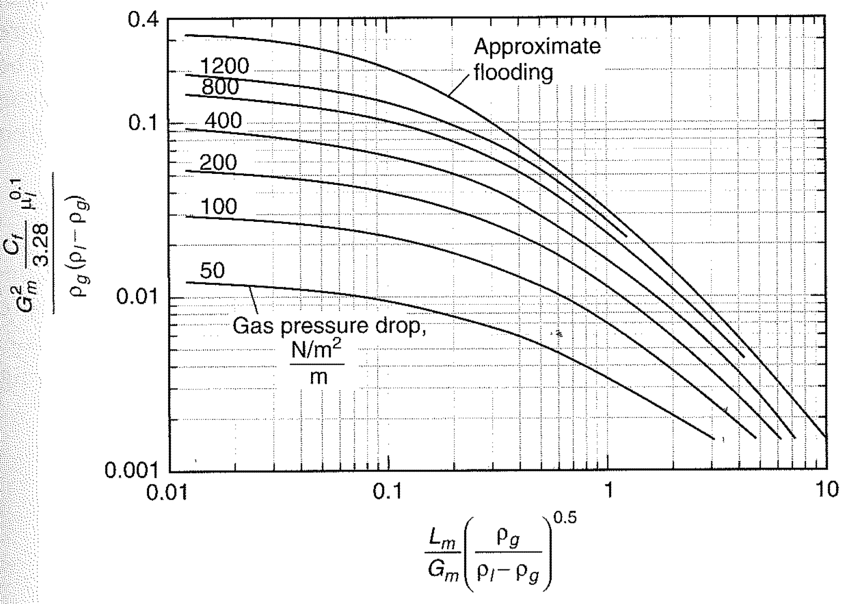


Figure 14-21
Generalized Eckert gas pressure drop and liquid and gas loading correlation in SI units for random packed tower. The coefficient 3.28 is a conversion factor when the packing factor in SI units (m^{-1}) is used because the Eckert diagram was originally drawn in English units. (Adapted from Eckert, 1961; Treybal, 1980).

Table 18-5 *(Continued)*

Number	Reactions	Rate Constants at 25°C, $M^{-1}\ s^{-1}$	References
		Reactions Common for Both H_2O_2/O_3 and H_2O_2/UV Process	
9	$HO\cdot + HO_2^- \xrightarrow{k_9} OH^- + HO_2\cdot$	$k_9 = 7.5 \times 10^9$	Christensen et al. (1982)
10	$HO\cdot + H_2O_2 \xrightarrow{k_{10}} H_2O + HO_2\cdot$	$k_{10} = 2.7 \times 10^7$	Buxton and Greenstock (1988)
11	$HO\cdot + HCO_3^- \xrightarrow{k_{11}} CO_3^-\cdot + H_2O$	$k_{11} = 8.5 \times 10^6$	Buxton and Greenstock (1988)
12	$HO\cdot + R \xrightarrow{k_{12}}$ products	$k_{12}{}^b$	Buxton and Greenstock (1988)
13	$HO\cdot + NOM \xrightarrow{k_{13}}$ products	$k_{13} = 3 \times 10^8$ to 4.5×10^8 (average 3.9×10^8) L/mol C	Westerhoff et al. (1999)
		Acid Dissociation Constants	
14	$H_2CO_3^* \rightleftarrows H^+ + HCO_3^-$	$pK_{a1} = 6.3$	Stumm and Morgan (1981)
15	$HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$	$pK_{a2} = 10.3$	Stumm and Morgan (1981)
16	$H_2O \rightleftarrows H^+ + OH^-$	$pK_{a3} = 14$	Stumm and Morgan (1981)
17	$H_2O_2 \rightleftarrows H^+ + HO_2^-$	$pK_{a5} = 11.75$	Behar et al. (1970)
18	$HO_2\cdot \rightleftarrows H^+ + O_2^-\cdot$	$pK_{a6} = 4.8$	Staehelip and Hoigné (1982)

Table 18-2

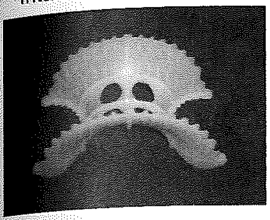
Reaction rate constants and half lives for degradation of selected inorganic and organic species by hydroxyl radicals[a]

Compound	HO· Rate Constant, L/mol · s	Half-Life, min		
		$[HO\cdot] = 10^{-9}$ M	$[HO\cdot] = 10^{-10}$ M	$[HO\cdot] = 10^{-11}$ M
Inorganics				
Ammonia	9.0×10^7	0.13	1.3	13
Bicarbonate	8.5×10^6	1.4	14	140
Bromide	1.1×10^{10}	0.001	0.01	0.1
Carbonate	3.9×10^8	0.03	0.3	3
Chloride	4.3×10^9	0.003	0.03	0.3
Iron(II)	3.2×10^8	0.04	0.4	4
Hydrogen peroxide	2.7×10^7	0.43	4.3	43
Manganese(II)	3.0×10^7	0.39	3.9	39
Ozone	1.1×10^8	0.11	1	11
Organics				
Acetate ion	7.0×10^7	0.2	2	17
Acetone	1.1×10^8	0.11	1.1	11
Atrazine	2.6×10^9	0.004	0.04	0.44
Benzene	7.8×10^9	0.001	0.01	0.1
Chloroacetic acid	4.3×10^7	0.3	2.7	27
Chlorobenzene	4.5×10^9	0.003	0.03	0.3
Chloroform	5.0×10^6	2	23	231
2-Chlorophenol	1.2×10^{10}	0.001	0.01	0.1
Formate ion	2.8×10^9	0.004	0.0	0
Geosmin	$(1.4 \pm 0.3) \times 10^{10}$	0.00083	0.0083	0.083
Methyl ethyl ketone	9.0×10^8	0.01	0.1	1
Methyl *tert*-butyl ether	1.6×10^9	0.01	0.1	1
MIB	$(8.2 \pm 0.4) \times 10^9$	0.0014	0.014	0.14
Natural organic matter	1.4 to 4.5×10^8	0.03	0.3	3.0
Oxalic acid	1.4×10^6	8	83	825
Oxalic ion	1.0×10^7	1	12	116
p-Dioxane	2.8×10^9	0.004	0.04	0.4
Phenol	6.6×10^9	0.002	0.02	0.2
Tetrachloroethylene	2.6×10^9	0.004	0.04	0.4
1,1,1-Trichloroethane	4.0×10^7	0.3	3	29
1,1,2-Trichloroethane	1.1×10^8	0.11	1	11
Trichloroethylene	4.2×10^9	0.003	0.03	0.3
Trichloromethane	5.0×10^6	2	23	231
Urea	7.9×10^5	15	146.2	1462
Vinyl chloride	1.2×10^{10}	0.001	0.01	0.1

[a] Additional values are available in the electronic Table E-4 at the website listed in App. E.

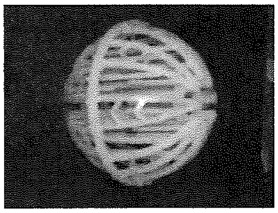
Source: Adapted from Buxton and Greenstock (1988), Lal et al. (1988), and Mao et al. (1991).

Intalox Saddles



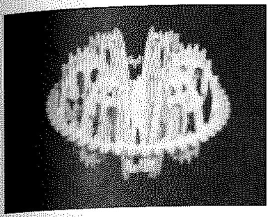
d_p	5.08 cm (2.0 in.)	7.62 cm (3.0 in.)
C_f	69 m^{-1} (21 ft^{-1})	52 m^{-1} (16 ft^{-1})
a_t	98 m^{-1} (30 ft^{-1})	66 m^{-1} (20 ft^{-1})

Jaeger Tri-Packs



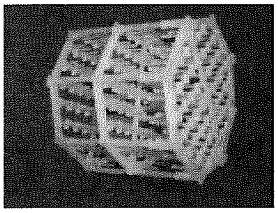
d_p	5.08 cm (2.3 in.)	8.89 cm (3.5 in.)
C_f	52 m^{-1} (16 ft^{-1})	39 m^{-1} (12 ft^{-1})
a_t	157 m^{-1} (48 ft^{-1})	125 m^{-1} (38 ft^{-1})

Tellerettes (Type K)



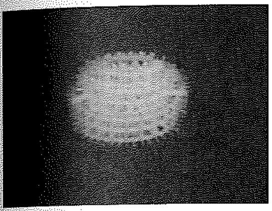
	No. 2	No. 3
d_p	5.08 cm (2.0 in.)	7.62 cm (3.0 in.)
C_f	36 m^{-1} (11 ft^{-1})	30 m^{-1} (9 ft^{-1})
a_t	52 m^{-1} (28 ft^{-1})	72 m^{-1} (22 ft^{-1})

Lantec Q-PAC



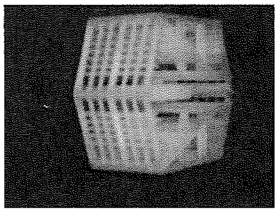
d_p	8.89 cm (3.5 in.)	
C_f	23 m^{-1} (7 ft^{-1})	
a_t	98 m^{-1} (30 ft^{-1})	

Lantec NUPAC



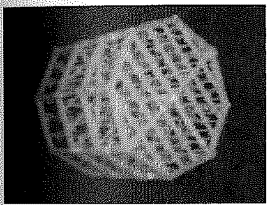
d_p	6.32 cm (2.5 in.)	11.4 cm (4.5 in.)
C_f	53 m^{-1} (16 ft^{-1})	26 m^{-1} (8 ft^{-1})
a_t	180 m^{-1} (55 ft^{-1})	131 m^{-1} (40 ft^{-1})

Lantec LANPAC



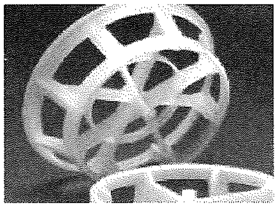
d_p	5.84 cm (2.3 in.)	8.89 cm (3.5 in.)
C_f	69 m^{-1} (21 ft^{-1})	46 m^{-1} (14 ft^{-1})
a_t	223 m^{-1} (68 ft^{-1})	144 m-1 (44 ft-1)

Lantec LANPAC-XL



d_p	8.89 cm (3.5 in.)	
C_f	33 m^{-1} (10 ft^{-1})	
a_t	242 m^{-1} (74 ft^{-1})	

Plastic rings



d_p	5.08 cm (2.0 in.)	7.62 cm (3.0 in.)
C_f	82 m^{-1} (25 ft^{-1})	30 m^{-1} (9 ft^{-1})
a_t	108 m^{-1} (33 ft^{-1})	72 m-1 (22 ft-1)

Critical surface tension depends on material, for polypropylene, $\sigma_c = 0.033$ N/m

Figure 14-12
Typical examples of polyethylene packing materials used in air-stripping towers and their physical characteristics.

1. (50 pts) Imagine that you are going to use **adsorption onto activated carbon** to remove EDB from water at 25 °C. You have to choose from three different types of activated carbon (type A, type B, or type C). EDB exhibits a different sorption isotherm for each of the three types of carbon. Also, the price of the carbon differs. Here are the three choices for carbon, along with the costs and the Freundlich isotherm parameters for EDB.

	Carbon A	**Carbon B**	**Carbon C**
K_F (μg/g) / (μg/L)$^{1/n}$	101	235	419
$1/n$	0.894	0.702	0.513
cost per kg	$ 3.49	$ 2.99	$ 3.24

   a. (12 pts) Suppose you are going to treat a stream of water that contains EDB at a concentration of 900 μg/L. The flow rate of the contaminated stream is 380 L/min. You want to reduce the concentration to 5 μg/L or lower. For this part of the problem, assume you are going to use a fixed bed of granular activated carbon (GAC). (Actually you will use two beds operating in series, so you don't have to worry about the width of the mass-transfer zone). Which of the three types of carbon will you choose to minimize your cost? Show your calculations to support your decision.

   b. (12 pts) Now suppose that the concentration of EDB in the stream of contaminated water drops from 900 μg/L to 100 μg/L. The flow rate does not change. Is there any reason to switch to a different carbon, or would you keep using the same one? If you switch, to which one? Show your calculations to support your decision.

   c. (12 pts) Now suppose that instead of a fixed bed of GAC, you will treat the water by adding powdered activated carbon (PAC) to a completely mixed flow reactor. You might do this, for instance, if the EDB contamination is an intermittent problem rather than a continuous problem. Assume that the concentration of EDB in the contaminated stream is 900 μg/L, and you want to treat it to 5 μg/L or lower, similar to part (a). Also assume that the residence time in the CMFR is long enough that the system reaches equilibrium. Now which type of carbon would you select? (The isotherms for the GAC and the PAC are the same.) Show your calculations to support your decision.

   d. (7 pts) Continue your PAC operation from part (c). Now, however, suppose that the influent concentration of the water drops from 900 μg/L to 100 μg/L (as in part b). Is there any reason to switch to a different carbon, or would you keep using the same one? If you switch, to which one? Why? Explain or show calculations as necessary.

   e. (7 pts) Briefly explain the choices you made in parts (a)–(d). Did you make similar choices for the GAC and the PAC? Why or why not?

2. (50 pts) Imagine that you are investigating if **air stripping** (packed tower aeration) is a good method for removing EDB from water at 25 °C. For this problem, the concentration of EDB in the contaminated water is 200 μg/L. We have the following design for an air-stripping tower.

Tower diameter, $d = 1.0$ m
Packing height, $L = 8.0$ m
Packing type = 2-inch plastic rings

Liquid loading rate, $L_M = 10.0$ kg/(m^2•s)
Gas loading rate, $G_M = 0.50$ kg/(m^2•s)
Pressure drop, $\Delta P/L < 50$ Pa/m

From the Onda correlation: $k_L = 2.2\times10^{-4}$ m/s, $k_G = 1.0\times10^{-2}$ m/s, $a_w = 58$ m^2/m^3

a. (8 pts) Estimate/calculate the water flow rate and the air flow rate, both in units of m^3/s.
b. (8 pts) Estimate/calculate Henry's constant, H, for EDB at 25 °C. Report H in its dimensionless form. Be sure to take care of your units!
c. (6 pts) Estimate/calculate the stripping factor, S, for EDB in this system.
d. (8 pts) Estimate/calculate the height of a transfer unit, HTU, under these conditions.
e. (12 pts) Estimate/calculate C_e, the concentration of EDB in the water stream that exits the bottom of the air-stripping tower. How much fractional removal of EDB do we get in this air stripping unit? Hint: you are given the packing height L and you just calculated HTU.
f. (8 pts) Suppose that we want to achieve a treatment objective of 5 μg/L. Is this goal achieved under the specified conditions? If not, what appears to be the main impediment to achieving the treatment objective? Based on that, is there some process change that might enable us to achieve the treatment objective? Try to be specific, if you can.

3. (50 pts) You are employing **advanced oxidation by ozone and peroxide** for the removal of EDB from water. The process takes place in a single-stage completely mixed flow reactor (CMFR). Ozone is bubbled into the bottom of the reactor, and hydrogen peroxide (H_2O_2) is dosed into to the contaminated water just before it enters the reactor. This results in the formation of $^{\bullet}$OH radicals to destroy the EDB. The conditions in the reactor are as follows.

   Temperature, T = 25 °C
   Hydraulic residence time, τ = 15 min
   Influent EDB concentration, C_I = 200 μg/L
   Partial pressure of ozone in the gas stream, P_{O3} = 0.040 atm
   Henry's constant for ozone gas at 25 °C, H_{PC} = 89.1 atm•L/mol
   Overall mass transfer coefficient for ozone delivery, $K_La = 4.0 \times 10^{-4}\ s^{-1}$
   pH of contaminated water = 7.0
   Concentration of bicarbonate, $[HCO_3^-]$ = 183 mg/L = 3.0×10^{-3} mol/L
   Concentration of dissolved organic carbon, [NOM] = 0.24 mg/L = 2.0×10^{-5} mol/L
   Concentration of peroxide, $[H_2O_2]$ = 1.7 mg/L = 5.0×10^{-5} mol/L
   Concentration of ozone, $[O_3]$ = 1.3 mg/L = 2.7×10^{-5} mol/L
   Concentration of hydroxyl radicals, $[^{\bullet}OH] = 4.0 \times 10^{-12}$ mol/L

   Under these conditions, the effluent concentration of EDB is C_E = 100 μg/L. This means we are removing 50% of the incoming EDB.

   a. (10 pts) Estimate/calculate the value of k_2, the second-order reaction rate coefficient, for the destruction of EDB by $^{\bullet}$OH. Be sure to report the proper units. Hint: what is C_E/C_I for a CMFR?

   Unfortunately, it has been determined that the current performance is unacceptable, and better removal of EDB is required. Three possible process changes have been suggested. For parts (b)–(d) below, *estimate the effluent concentration of EDB that will result* if the proposed process modification is implemented. NOTE: you probably can't get an exact answer without going through a complicated iterative process like you did on HW8, and that isn't feasible for this exam; instead, make your best estimates, show your calculations, and/or explain your reasoning, as needed.

   b. (10 pts) The ceramic diffusers in the reactor are upgraded so that the overall mass-transfer coefficient for ozone doubles to $K_La = 8.0 \times 10^{-4}\ s^{-1}$.

   c. (15 pts) A softening system is put in upstream of the reactor, which reduces the bicarbonate concentration in the reactor to 12.2 mg/L = 2.0×10^{-4} mol/L.

   d. (10 pts) The ozone generation system is upgraded so that the partial pressure of ozone in the gas stream increases to 0.080 atm.

   e. (5 pts) Which option offers the best improvement? Why? Briefly (a few sentences) explain the principle behind the best improvement and why it is superior to the other two options.

END OF EXAMINATION