ENV 6519: Physical & Chemical Processes for Groundwater Remediation

Spring 2021 | University of South Florida
Homework #3 | Civil & Environmental Engineering
Due Thursday, Feb. 4, 2021 | J.A. Cunningham

(1) (20 pts) (*adapted from a problem written by Prof Paul V Roberts of Stanford University*) Equilibrium data are given below for the adsorption of paranitrophenol (PNP, molecular weight = 139 g/mol) from aqueous solution at 20 °C by Calgon Filtrasorb 400 carbon. The data were obtained by adding different carbon mass to beakers containing 100 mL of aqueous PNP solution with an initial concentration of 1.0 mM, then measuring the aqueous concentration after sufficient time had passed to reach equilibrium.

Beaker #	Mass of carbon added (mg)	PNP concentration at equilibrium (mM)
1	105	0.004
2	83	0.007
3	79	0.012
4	70	0.021
5	60	0.042
6	53	0.080
7	53	0.092
8	42	0.170
9	34	0.290
10	27	0.430

(a) (12 pts) Using units of mmol/L and mmol/g, estimate the constant (K_F) and the exponent ($1/n$) for a Freundlich isotherm applied to these data. Hint: you will have to calculate the sorbed concentration in each beaker. A spreadsheet in Excel would probably help you. Watch your units!

(b) (5 pts) What would be the values of K_F and $1/n$ if you converted to units of mg/L and mg/g instead of mmol/L and mmol/g?

(c) (3 pts) How favorable or unfavorable is the isotherm? Explain (in about a sentence).

(2) (20 pts)

(a) (10 pts) Complete problem 15-6 in your text. Which isotherm do you think fits the data better, Langmuir or Freundlich?

(b) (10 pts) Complete problem 15-7 in your text. How does your estimated value of $1/n$ compare to the values from problem 15-6 and Table 15-7?

(3) (20 pts) The following papers will be made available to students in the class:

Crittenden JC, Luft P, Hand DW, 1985. Prediction of multicomponent adsorption equilibria in background mixtures of unknown composition. *Water Research*, 19(12), 1537–1548.

Speth TF and Miltner RJ, 1990. Technical note: adsorption capacity of GAC for synthetic organics. *Journal AWWA*, 82(2), 72–75.

(a) (7 pts) In Table 3 of the Crittenden paper, the authors report the Freundlich isotherm parameters for the adsorption of seven contaminants onto Calgon F-400 carbon. All seven of those contaminants were also considered by Speth and Miltner. Choose any three of the seven compounds. For those compounds, tabulate the K_F and $1/n$ values reported by the two different papers. Use units of μg/L for aqueous conc. and μg/g for sorbed conc.

(b) (7 pts) For each of the three compounds, plot the sorption isotherms as q (μg/g) versus C (μg/L) using the Freundlich coefficients that you tabulated in part (a). Plot the graphs for an aqueous concentration range up to 1.0 mg/L for each compound. You should make three separate graphs, one for each chemical. On each graph, you should have two curves, corresponding to the two estimates of K_F and $1/n$ for each compound.

(c) (6 pts) Based on the graphs, how well do the values agree between the two sources? Did the two groups obtain pretty similar values of K_F and $1/n$, or pretty different? If there are significant discrepancies, why might that be so? Think about what this means for your design project. If you find conflicting estimates of Freundlich isotherms, which values should you use for your design calculations? Why?

(4) (40 pts) The following report will be made available to students in the class:

Dobbs RA, Cohen JM, 1980. *Carbon Adsorption Isotherms for Toxic Organics*. United States Environmental Protection Agency report no. EPA-600/8-80-023. U.S. Environmental Protection Agency: Cincinnati, OH.

Also, this problem includes some chemical data, which are from the following references:

Schwarzenbach RP, Gschwend PM, Imboden DM, 2003. *Environmental Organic Chemistry*, 2nd ed. Wiley-Interscience: Hoboken, NJ.

National Library of Medicine. *Compound summary: 1,2-Dibromo-3-chloropropane*. https://pubchem.ncbi.nlm.nih.gov/compound/1_2-Dibromo-3-chloropropane

Problem 4 continues →

4. continued

(a) (4 pts) Look up the adsorption data for bromodichloromethane (BDCM) onto Calgon F-300 carbon according to the EPA report. The report gives the isotherm data, both aqueous concentrations (in units of mg/L) and adsorbed concentrations (in units of mg/g), on page 143. (Note that the EPA report calls it dichlorobromomethane, but that is the same thing as bromodichloromethane.) Convert the adsorbed concentrations into W, the volume sorbed per mass of carbon. Use units of cm^3 adsorbed per g of carbon. The liquid density of BDCM is given in a table on the next page.

(b) (4 pts) Convert the aqueous concentrations into Polanyi potentials, ε. Use units of J/mole for ε. The aqueous solubility of BDCM is given in a table on the next page. Assume that the experiments were performed at 23 °C (I am not sure if this is correct, but it should be close).

(c) (4 pts) Divide the Polanyi potentials by V_m, the molar volume of BDCM. Use units of cm^3/mole for V_m, so that ε/V_m ends up with units of J/cm^3. The molar volume can be estimated as the molar mass (g/mole) divided by the liquid density (g/cm^3). Note that V_m is slightly different from V_b that you used on the previous homework assignment…V_b is the molar volume at the normal boiling point. The two numbers are close but not exactly the same.

(d) (5 pts) Graph W versus ε/V_m. Your graph should have seven data points. Make the ordinate axis logarithmic. Then, fit the following line through the data:

$$W = W_0 \exp(-\beta * \varepsilon/V_m)$$

You might be able to get Excel to provide this fit for you. If not, then you can find the best-fit values of W_0 and β by using the log-transformed version of the equation:

$$\ln(W) = \ln(W_0) - \beta*(\varepsilon/V_m)$$

Note that your best-fit line should look like a straight line because you made the ordinate axis logarithmic. If your best-fit line doesn't look like a straight line, then you did something wrong. Report the best-fit values of W_0 (in units of cm^3/g) and β (in units of cm^3/J). In theory, W_0 and β are properties of the sorbent (i.e., the carbon) but do not depend on the sorbate.

(e) (3 pts) The equation that you used in part (d) comes from Polanyi potential theory, but assumes that the parameter σ (a property of the activated carbon employed) is equal to exactly 1. If the line fits the data quite well, then this is probably a good assumption. If the line does not fit the data well, then it is probably a bad assumption. What do you think? Based on the BDCM data, is it OK to assume that $\sigma = 1$ for Calgon F300?

Problem 4 continues →

4. continued

(f) (5 pts) Compare your estimated W_0 and β for Calgon F300 to the values given in Table 15-8 of your text. How closely do they agree? If the agreement is poor, I am not sure which is more reliable, the table in the text, or the data in the EPA report. (The EPA study used a short equilibration time, which makes their data a little suspect, but still the experimental data might be more reliable than the table in the text; I do not know.) For the remaining parts of this problem, use your estimated values of W_0 and β, *not* the text-book values.

(g) (8 pts) From your estimated W_0 and β, estimate the Freundlich parameters for the sorption of trichloroethene (TCE) and 1,2-dibromo-3-chloro-propane (DBCP) onto F300 carbon at 23 °C. (Hint: see p 1151 of your text.) Report K_F and $1/n$ for both chemicals. Make sure K_F is in units corresponding to mg/g and mg/L. Assume that the Polanyi parameter $\sigma = 1.0$ (you implicitly made this assumption in part d, above). From Schwarzenbach et al. (2003) and from the NIH web site, we have the following data.

Chemical	**Molar mass (g/mole)**	**Liquid density (g/mL)**	**Aqueous solubility (mole/L)**	**Aqueous solubility (mg/L)**
trichloroethene (TCE)	131.4	1.46	$10^{-2.08}$	
bromodichloro-methane (BDCM)	163.8	1.97	$10^{-1.55}$	
1,2-dibromo-3-chloropropane (DBCP)	236.3	2.05		1230

(h) (3 pts) Compare your estimated Freundlich parameters for TCE and DBCP to the experimentally determined parameters reported by Dobbs and Cohen (p 294 for TCE, p 132 for DBCP). How closely do they agree? (Qualitative discussion is OK.)

(i) (4 pts) Now let's examine the point of all these seemingly esoteric calculations!! Imagine that somebody found the chemical 1,1,2,2-tetrachloroethane in groundwater, and they'd like to clean up the water -- as in your design project this semester. As an environmental engineer, you are wondering if Calgon F300 activated carbon might be a viable alternative for removing this chemical from the water. Unfortunately, the EPA report of Dobbs and Cohen did not report an isotherm for this chemical. You could spend a month in the lab measuring the isotherm on Calgon F300, but perhaps there is an easier way. Discuss how Polanyi potential theory might be helpful to you in making your engineering decision. (By the way, Schwarzenbach et al. (2003) do report the physical properties for this chemical on pg 1200, so you could go through the exercise for 1,1,2,2-tetrachloroethane if you wish!)