ENV 6002: Physical & Chemical Principles of Environmental Engineering

Fall 2021 | University of South Florida
Homework #3 | Civil & Environmental Engineering
Due Tuesday, Sept. 21, 2021 | J.A. Cunningham

(1) (15 pts) Answer Problem 6-1 in your text book (p 414). Hint 1: look up the density of carbon tetrachloride so you know what mass was added to the system. Hint 2: what else will you need to look up for each chemical? Hint 3: this problem is pretty similar to the last problem from homework #2.

(2) (20 pts) Answer problem 6-8 in your text book (p 418). I will talk you through it.

- The problem tells you the initial aqueous concentration (before the activated carbon is added) and the equilibrium aqueous concentration (after the water equilibrates with the activated carbon).
- The problem does not tell you the concentration of MIB in the adsorbed phase. You have to calculate that from the data given.
- The adsorbed concentration can be calculated as $\Delta C/D_0$. That would give you units μg/mg. You probably want to convert the adsorbed concentrations to units of μg/g, which is a more standard unit for reporting adsorbed concentrations.
- Once you have the adsorbed concentrations, you must find the best-fit parameters for the Freundlich isotherm and for the Langmuir isotherm.
- The Langmuir isotherm is equation 6-58 in your text, but to find the best-fit parameters Q and b, use one of the alternate forms given in 6-59, 6-60, or 6-61. That will enable you to perform linear regression. Equation 6-59 is the most common way to do it, though personally I prefer equation 6-60. For whichever form you choose, you must ask yourself: to get a straight line, I should graph ____ versus ____?
- The Freundlich isotherm is equation 6-67 in your text. To find the best-fit parameters K_F and n, use the alternate form 6-68. This will enable you to use linear regression. To get a straight line, you should graph ____ versus ____?
- For both the Langmuir isotherm and the Freundlich isotherm, watch your units carefully. The units on the Freundlich isotherm are particularly strange. The coefficient n is dimensionless, but the capacity factor K_F has very weird units.

(3) (20 pts) *based on a problem originally written by Paul Roberts of Stanford University*

(a) Look up the octanol-water partition coefficient for 1,1,1-trichloroethane (TCA). Then estimate K_d for the partitioning of TCA to a solid phase, assuming that the solid phase is 20% organic carbon by mass. Use the "all-purpose" relationship of Karickhoff to estimate K_{oc}. Be sure to specify the units of K_d.

(b) Suppose that the density of the solid phase is 1.1 g/cm^3 = 1.1 kg/L. Estimate/calculate a *dimensionless* partitioning constant, K_P, that describes the partitioning of TCA between the water phase and the sorbed phase, if we represent the sorbed concentration on a mass/volume basis. That is, estimate K_P such that

$C_i^{solid} = K_P\ C_i^{water}$

and both C_i^{solid} and C_i^{water} are in the same units of mg/L.

Hint: think carefully about the units of K_d and the units of K_P. It is possible to derive a very useful (and simple) relationship between K_d and K_P.

(c) Suppose you have a column of water with some suspended particulate matter. The particulate matter has a density of 1.1 g/cm^3, as above. The particulate matter occupies 0.01% of the total volume of the system (so the water occupies 99.99%). There is TCA in the system, and the system has reached equilibrium. Estimate *the fraction of TCA mass* in each phase (i.e., in the water phase and in the suspended solids). Hint 1: the fractions must add up to 1. Hint 2: what is the relationship between *mass ratio*, *volume ratio*, and *concentration ratio*?

(d) Now suppose that you had a sediment. The sediment contains both a solid phase (i.e., the solid grains) and a water phase (which fills the pores between the solid grains). The solid phase occupies 60% of the total volume; or, in other words, the porosity of the sediment is 40%. The solid grains have density 1.1 g/cm^3 as above. There is TCA in the system, and the system has reached equilibrium. Estimate the fraction of TCA mass in each phase (i.e., in the water phase and absorbed by the solid phase).

(e) Discuss your answers to parts (b), (c), and (d) in terms of the differences between *concentration ratios* and *mass ratios*.

(4) (15 pts) *based on a problem originally written by Paul Roberts of Stanford University*

A closed bottle contains 10 mL air and 90 mL water at 25 C. Suspended in the water is 36 mg of particulate (i.e., solid) matter that has a specific gravity of 1.00. The mass fraction of organic carbon in the suspended particulate is 0.10. The bottle contains 10 mg of tetrachloroethylene, C_2Cl_4, also called perchloroethylene, or PCE. Estimate/calculate the fraction of PCE mass in the water, in the air, and in the suspended solids. Use the "all-purpose" relationship of Karickhoff to estimate K_{oc}.

(5) (15 pts) *based on a problem originally written by Paul Roberts of Stanford University*

It has been observed experimentally that when methanol partitions between water and air under ambient (but sufficiently dilute) conditions, Henry's constant H_{yx} = 0.30. It is also known that the vapor pressure of methanol at 298 K is 0.191 atm.

(a) Based on this information, estimate/calculate the activity coefficient for methanol in water. Hint: use fugacity relationships, and think about what Hyx means.

(b) Based on the activity coefficient that you found in part (a), would you categorize methanol as hydrophobic or hydrophilic? Explain briefly.

(c) Assume that the activity coefficient of methanol in octanol is very close to 1.0, because methanol and octanol are both alcohols. Based on this assumption, and your result from part (a), estimate the octanol-water partition coefficient for methanol. Hint 1: use fugacity relationships to estimate a ratio of mole fractions, then convert the mole fractions into concentrations. Hint 2: the density of octanol is 826 g/L and the molecular formula for octanol is $C_8H_{17}OH$.

(6) (15 pts) Answer problem 6-9 in your text book.