CE3501 Environmental Engineering
Part II. Environmental Biology
Fall 2005
Homework Assignment #2, Due Monday, 10/24 in class

1. Balance the following redox reactions:
   a. Sulfate reduction: $CH_20 + SO_4^{2-} \leftrightarrow HCO_3^- + HS^- + H^+$

   ANSWER: $2CH_2O + SO_4^{2-} \leftrightarrow 2HCO_3^- + HS^- + H^+$

   b. Nitrification: $NH_4^+ + O_2 \leftrightarrow NO_3^- + H_2O + H^+$

   ANSWER: $NH_4^+ + 2O_2 \leftrightarrow NO_3^- + H_2O + 2H^+$

   c. Iron reduction: $CH_2O + Fe(OH)_{3(s)} \leftrightarrow HCO_3^- + Fe^{2+} + OH^- + H_2O$

   ANSWER: $CH_2O + 4Fe(OH)_{3(s)} \leftrightarrow HCO_3^- + 4Fe^{2+} + 7OH^- + 3H_2O$

   d. Aerobic oxidation of MTBE: $C_5H_{12}O + O_2 \leftrightarrow CO_2 + H_2O$

   ANSWER: $C_5H_{12}O + 7.5O_2 \leftrightarrow 5CO_2 + 6H_2O$

You may use either the method of half-reactions or balance the whole reaction equation.

2. Write and balance the half-reactions (oxidation, reduction) for the following reactions:
   a. Manganese reduction: $CH_2O + MnO_2 + H^+ \leftrightarrow HCO_3^- + Mn^{2+} + H_2O$

ANSWER: Oxidation: $CH_2O + 2H_2O \rightarrow HCO_3^- + 5H^+ + 4e^-$
Reduction: $2MnO_2 + 8H^+ + 4e^- \rightarrow 2Mn^{2+} + 4H_2O$
OVERALL: $CH_2O + 2MnO_2 + 3H^+ \leftrightarrow HCO_3^- + 2Mn^{2+} + 2H_2O$

   b. Denitrification: $NO_3^- + CH_2O \rightarrow N_2 + HCO_3^- + H^+ + H_2O$

ANSWER: Oxidation: $5CH_2O + 10H_2O \rightarrow 5HCO_3^- + 25H^+ + 20e^-$
Reduction: $4NO_3^- + 24H^+ + 20e^- \rightarrow 2N_2 + 12H_2O$
OVERALL: $5CH_2O + 4NO_3^- \rightarrow 5HCO_3^- + 2N_2 + H^+ + 2H_2O$

3. What is the theoretical oxygen demand (ThOD) for complete oxidation of a saturated solution of the pesticide malathion? The solubility of malalthion is 144 mg/L. (**223 mg/L**)

$$C_{10}H_{19}O_6PS_2 + 16O_2 \rightarrow 10CO_2 + H_2PO_4^- + 2SO_4^{2-} + 5H^+ + 6H_2O$$

SOLUTION:
Step 1 (balancing the reaction equation) has already been done for you.

Step 2. Ratio of O_2 to malathion

$$\frac{16 moles O_2}{mole Malathion} \bullet \frac{32 g O_2}{mole O_2} \bullet \frac{mole Malathion}{330 g} = 1.55 \frac{g O_2}{g Malathion}$$

Step 3. Convert starting concentration of Malathion to ThOD

$$144 \frac{mg Malathion}{L} \bullet 1.55 \frac{mg O_2}{mg Malathion} = 223 \frac{mg O_2}{L}$$

4. What is the average oxidation state of carbon in malathion ($C_{10}H_{19}O_6PS_2$)? The oxidation state of the sulfur is -2 and that of phosphorus is +5. (**Ans: -0.8**)

ANSWER:

The molecule is uncharged so the sum of the products of oxidation state and numbers of atoms must equal zero.

10X + 19x(+1) + 6x(-2) + 1x(+5) + 2x(-2) = 0

10X = -8

X = -0.8

Therefore the average oxidation state of the 10 C atoms is + 0.8.

5. A tank truck of milk runs off of a bridge and dumps its entire contents (16 m^3) into a river. If the k_L for degradation of the milk is 0.4 d^{-1}, how long would be required to reduce the BOD in the river by 99% of the value at the spill site? Assume no tributaries or other water sources dilute the milk in the river as it flows downstream from the spill site. (**ANS: 11.5 d**)

SOLUTION:

The questions asks how long is required to reduce the original BOD (L_0) to 1% of its initial value. The relationship between L_t and L_0 is:

$$L_t = L_0 e^{-k_L t}$$

Therefore, this is simply first-order kinetics.

$$t = \frac{-1}{k_L} \bullet \ln\left(\frac{L_t}{L_0}\right) = \frac{-1}{0.4 d^{-1}} \bullet \ln\left(\frac{0.01 L_0}{L_0}\right)$$

$$t = 11.5 d$$

6. How much oxygen is *actually* consumed during decomposition of a waste depends on the extent to which the waste is biodegradable, i.e. amenable to oxidation by microbes. Ammonia is totally biodegradable and thus the nitrogenous ThOD (theoretical) and the nitrogenous BOD (actual) are equal. Not so for carbonaceous compounds; the carbonaceous BOD (actual) may be significantly less than the carbonaceous ThOD (theoretical) if the compound is poorly degradable. The 5-day BOD test provides an estimate of the amount of oxygen that a waste will actually consume. The malathion waste in Problem 3 was found to have a 5-day BOD of 125 mg/L and a rate constant (k_L) of 0.2 d^{-1}. Calculate the ultimate BOD of the solution**.** Is the malathion very biodegradable? What fraction of the potential oxidation actually occurs? **(198 mgO_2/L,**

Yes, 88%).

SOLUTION:

$BOD_5 = y_5 = 125$ mg/L

$k_L = 0.2\ d^{-1}$

$$y_t = L_0 - L_t = L_0\left(1 - e^{-k_L t}\right)$$

$$L_0 = \frac{y_t}{\left(1 - e^{-k_L t}\right)} = \frac{125\frac{mg}{L}}{1 - e^{-0.2d^{-1}\cdot 5d}} = 198\frac{mg}{L}$$

Thus, the ultimate BOD (L_o) is 198 mg/L. This represents 88% of the ThOD (223 mg/L), and it appears as if the Malathion is fairly biodegradable.