CEE 483 Winter 2009 HW#6 Solution

1. (a) i. The chlorine residual is mostly combined (present as chloramines) at doses less than the breakpoint. The curve shown never has a residual of 3 mg/L as such doses, so the combined residual is never 3 mg/L. (There was a typo in the question. I meant to ask for the dosages at which the combined chlorine residual was 2.0 mg/L. In that case, the correct answer would have been doses of 3.6 and 5.3 mg/L.)

ii. The chlorine demand is the difference between the dose and the residual. The demand is 6 mg/L at an approximate dose of 6.9 mg/L, at which point the residual is approximately 0.9 mg/L.

iii. The free residual is greater than the combined residual at virtually any dose beyond the breakpoint, i.e., at doses >8.3 mg/L.

iv. Virtually any chlorine that is not measured as a residual has been converted to Cl^-, so >80% of the dose is converted to Cl^- when the chlorine residual is <20% of the dose. This criterion is met at doses less than approximately 1.0 mg/L, and again between doses of approximately 6.5 mg/L (when the residual is ~1.3 mg/L) and 10.8 mg/L (when the residual is ~2.2 mg/L). At higher doses, the residual increases by almost exactly the same amount as the dose, and the residual is once again >20% of the dose.

v. The free residual is increasing with chlorine dose at any dose greater than the breakpoint dose (i.e., at doses > 8.3 mg/L as Cl_2); in truth, the increase starts at slightly lower doses.

(b) The chlorine demand is the difference between the dose and the residual. At a dose of 7 mg/L, the residual is about 0.8 mg/L, so the demand is 6.2 mg/L as Cl_2.

2. The molecular weights of the model NOM molecule and ozone are:

$C_{24}H_{24}O_{12}$ 24*12 + 24*1 + 12*16 = 504

O_3: 3*16 = 48

To balance the oxidation reaction, we first note that, by a charge balance on the molecules, the charge (oxidation number) on carbon in the NOM molecule is 0, and that on the carbon in oxalate is +3. Thus, each carbon atom loses 3 electrons when NOM is oxidized to oxalate. The charge on the oxygen in ozone molecules is 0, and that on the oxygen in oxalate is −2, so each oxygen atom gains two electrons in the reaction. We can choose the stoichiometric coefficient for NOM to be 1, in which case the stoichiometric coefficient on oxalate must be 12, since all the carbon in NOM must be converted to carbon in oxalate. Thus, at this point, we have the following:

$$1\ C_{24}H_{24}O_{12} + \underline{??}\ O_3 \leftrightarrow 12\ C_2HO_4^- + ??$$

Since 24 carbon atoms are oxidized, and each one releases 3 electrons, 72 electrons are released, all of which are acquired by oxygen. Each oxygen in an ozone molecule gains two electrons, so 36 oxygen molecules must react, corresponding to 12 ozone molecules. Therefore, we can write:

$$1\ C_{24}H_{24}O_{12} + 12\ O_3 \leftrightarrow 12\ C_2HO_4^- + ??$$

We next balance the oxygen atoms by adding H_2O to either side of the reaction. In the current case, we have 48 oxygen atoms on each side of the reaction, so no H_2O is needed. Finally, we balance H atoms. There are 24 H atoms on the left and only 12 on the right, so we need to add 12 H^+ to the right side:

$$1\ C_{24}H_{24}O_{12} + 12\ O_3 \leftrightarrow 12\ C_2HO_4^- + 12\ H^+$$

Checking the charge balance, we see that each side of the reaction has a net zero charge, so charge is balanced, and we are done balancing the reaction.

An ozone demand of 15 mg/L means that 15 mg/L of ozone is consumed. In molar units, this corresponds to:

$$\frac{15\text{ mg/L O}_3}{48{,}000\text{ mol/L}} = 3.13\text{x}10^{-4}\,\frac{\text{mol O}_3}{\text{L}}$$

The amount of NOM that reacts is one-twelfth as much as the ozone (on a molar basis), and the molecular weight of the NOM is 504, so:

$$\text{NOM reacted} = \left(3.13\text{x}10^{-4}\,\frac{\text{mol O}_3}{\text{L}}\right)\left(\frac{1\text{ mol NOM}}{12\text{ mol O}_3}\right)\left(\frac{504{,}000\text{ mg NOM}}{\text{mol NOM}}\right) = 13.1\frac{\text{mg NOM}}{\text{L}}$$

3. (a) The Cl_2 that is added reacts first with Fe^{2+}. This Cl_2 is converted to Cl^- and therefore leaves no residual. Once all the Fe^{2+} has been oxidized, the Cl_2 reacts with NH_3 to form chloramines, and each mg of Cl_2 reacting generates one mg of residual as Cl_2. The amount of Cl_2 required to react with the Fe^{2+} is:

$$\left(4\frac{\text{mg Fe}^{2+}}{\text{L}}\right)\left(\frac{1\text{ mol Fe}^{2+}}{56{,}000\text{ mg Fe}^{2+}}\right)\left(\frac{1\text{ mol Cl}_2}{2\text{ mol Fe}^{2+}}\right)\left(\frac{71{,}000\text{ mg Cl}_2}{\text{mol Cl}_2}\right) = 2.53\frac{\text{mg Cl}_2}{\text{L}}$$

Therefore, to generate 4 mg/L of combined residual, we need to add $(2.53 + 4.0)$, or 6.53 mg/L of Cl_2.

(b) To generate a residual of free chlorine, essentially all the NH_3 has to be oxidized. The amount of Cl_2 required for that reaction is:

$$\left(8.5\frac{\text{mg NH}_3}{\text{L}}\right)\left(\frac{1\text{ mol NH}_3}{17{,}000\text{ mg NH}_3}\right)\left(\frac{3\text{ mol Cl}_2}{2\text{ mol NH}_3}\right)\left(\frac{71{,}000\text{ mg Cl}_2}{\text{mol Cl}_2}\right) = 53\frac{\text{mg Cl}_2}{\text{L}}$$

Therefore, to generate 4 mg/L of free residual, we need to add 2.53 mg/L as Cl_2 to oxidize the Fe^{2+}, 53 mg/L as Cl_2 to oxidize the NH_3, and 4.0 mg/L as Cl_2 to provide the residual, for a total of 59.5 mg/L as Cl_2.

(c) Each mole of NaOCl can combine with two electrons, and the same is true of a mole of Cl_2. Therefore, the same number of moles of NaOCl is needed as the number of moles of Cl_2, and the mass concentration of NaOCl required would be:

$$\left(6.53\frac{\text{mg Cl}_2}{\text{L}}\right)\left(\frac{1\text{ mol Cl}_2}{71{,}000\text{ mg Cl}_2}\right)\left(\frac{1\text{ mol NaOCl}}{\text{mol Cl}_2}\right)\left(\frac{74{,}500\text{ mg NaOCl}}{\text{mol NaOCl}}\right)=6.85\frac{\text{mg NaOCl}}{\text{L}}$$

4. (a) According to the graph, when the reactor is operated with a t_d of 20 min, the Cl_2 residual 2.1 mg/L as Cl_2. Since the Cl_2 dose was 5.8 mg/L, the Cl_2 demand exerted is 3.7 mg/L as Cl_2.

(b) The value of *T* that must be used in the *CT* calculation is the time when 10% of the spike of tracer has exited the reactor, and 90% remains in the reactor. Therefore, for a CMR, t_{10} can be computed as follows:

$$\frac{c}{c(0)}=0.9=\exp\left(-\frac{t_{10}}{t_d}\right)$$

$$t_{10}=-t_d\ln(0.9)$$

The value of *C* for use in the *CT* calculation is the concentration in the effluent from the disinfection reactor. In the CMR of interest, t_d is 45 min, so t_{10} is 4.74 min. The concentration of chlorine in the effluent from the CMR is 1.5 mg/L, so *CT* is (1.5 mg/L)(4.74 min), or
7.11 mg-min/L.