

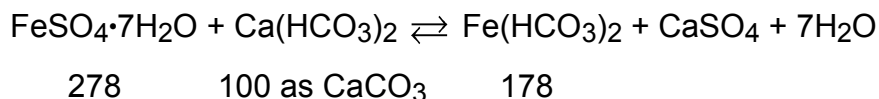
CHEMICAL UNIT PROCESSES

PROBLEM 6-1

Problem Statement - See text, page 544

Solution

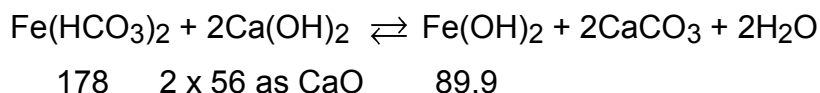
1. Determine the minimum alkalinity required for a ferrous sulfate dose of 25 g/m³ using Eq. (6-12).



Required alkalinity as CaCO₃

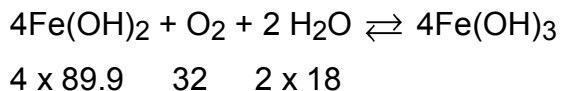
$$= \frac{100}{278} \times 25 \text{ g / m}^3 = 9.0 \text{ g / m}^3$$

2. Determine the amount of lime required as CaO using Eq. (6-14).



$$\text{Required lime as CaO} = \frac{178}{278} \times (25 \text{ g / m}^3) \left(\frac{2 \times 56}{178} \right) = 10.1 \text{ g / m}^3$$

3. Determine the amount of dissolved oxygen required using Eq. (6-15).



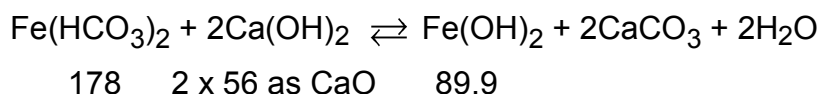
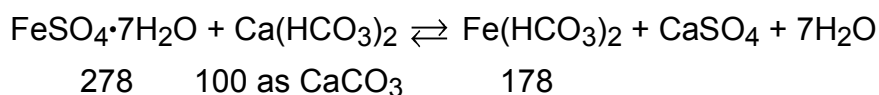
$$\text{Required DO} = \frac{89.9}{278} \times (25 \text{ g / m}^3) \left(\frac{32}{4 \times 89.9} \right) = 0.72 \text{ g / m}^3$$

PROBLEM 6-2**Problem Statement** - See text, page 544

Instructors Note: As a practical matter in discussing precipitation in wastewater it should be noted that about 15 g/m³ of CaCO₃ will remain in solution to satisfy the solubility product for CaCO₃. It should also be noted that the theoretical value calcium in solution computed using the solubility product given in Table 6-21 will be considerably lower.

Solution

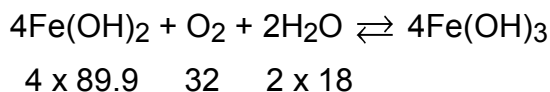
1. Determine the amount of lime required as CaO for a ferrous sulfate dose of 30 g/m³ using Eqs. (6-12) and (6-14).



Required lime as CaO (based on a FeSO₄·7H₂O dose of 30 g/m³) =

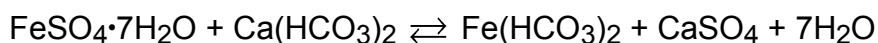
$$= \left[\frac{(178 \text{ g / mole})}{(278 \text{ g / mole})} \right] \left[\frac{2(56 \text{ g / mole})}{(178 \text{ g / mole})} \right] (30 \text{ kg / } 10^3 \text{ m}^3) = 12.1 \text{ kg / } 10^3 \text{ m}^3$$

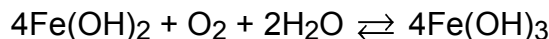
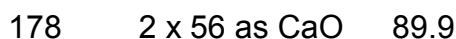
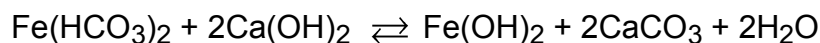
2. Determine the amount of dissolved oxygen required using Eq. (6-15).



$$\begin{aligned} \text{Required DO} &= \left[\frac{(89.9 \text{ g / mole})}{(278 \text{ g / mole})} \right] \left[\frac{(32 \text{ g / mole})}{4(89.9 \text{ g / mole})} \right] (30 \text{ kg / } 10^3 \text{ m}^3) \\ &= 0.9 \text{ kg / } 10^3 \text{ m}^3 \end{aligned}$$

3. Determine the amount of sludge produced per 10³ m³.
 - a. Determine the amount of Fe(OH)₃ formed using Eqs. (6-12), (6-14), and (6-15).



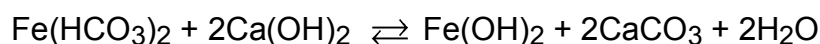


Amount of Fe(OH)_3 formed =

$$= \left[\frac{4(106.9 \text{ g/mole})}{4(89.9 \text{ g/mole})} \right] \left[\frac{(89.9 \text{ g/mole})}{(178 \text{ g/mole})} \right] \left[\frac{(178 \text{ g/mole})}{(278 \text{ g/mole})} \right] (30 \text{ kg} / 10^3 \text{ m}^3)$$

$$= 11.5 \text{ kg} / 10^3 \text{ m}^3$$

- b. Determine the amount of CaCO_3 formed.



Amount of CaCO_3 formed =

$$= \left[\frac{2(100 \text{ g/mole})}{(178 \text{ g/mole})} \right] \left[\frac{(178 \text{ g/mole})}{(278 \text{ g/mole})} \right] (30 \text{ kg} / 10^3 \text{ m}^3) = 21.6 \text{ kg} / 10^3 \text{ m}^3$$

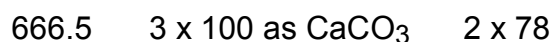
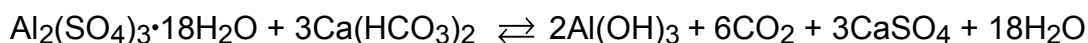
Assume that about 15 g/m^3 of CaCO_3 will remain in solution to satisfy the solubility product for CaCO_3 . It should be noted that the theoretical value computed for calcium using the solubility product given in Table 6-21 will be considerably lower.

- c. Determine the total amount of sludge produced

Sludge produced = Fe(OH)_3 + excess CaCO_3

$$\text{Sludge produced} = [11.5 + (21.6 - 15)] \text{ kg} / 10^3 \text{ m}^3 = 18.1 \text{ kg} / 10^3 \text{ m}^3$$

4. Determine the amount of alum needed (X) to obtain this same quantity of sludge using Eq. (6-9), assuming that Al(OH)_3 is the precipitate formed.



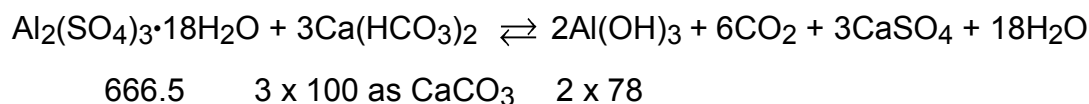
$$\left[\frac{2(78 \text{ g/mole})}{(666.5 \text{ g/mole})} \right] (X \text{ kg} / 10^3 \text{ m}^3) = 18.0 \text{ kg} / 10^3 \text{ m}^3$$

$$X \text{ kg} / 10^3 \text{ m}^3 = (18.0 \text{ kg} / 10^3 \text{ m}^3) \left[\frac{(666.5 \text{ g} / \text{mole})}{2(78 \text{ g} / \text{mole})} \right]$$

$$\text{Alum required} = 76.9 \text{ kg} / 10^3 \text{ m}^3$$

PROBLEM 6-3**Problem Statement** - See text, page 544**Solution – Part a**

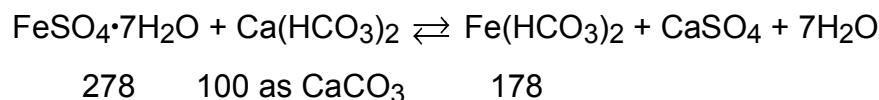
1. Determine the amount of $\text{Al}(\text{OH})_3$ sludge produced for an alum dose of 50 kg/4000 m^3 ($= 12.5 \text{ kg} / 10^3 \text{ m}^3$) using Eq. (6-9)



$$\begin{aligned} \text{Al}(\text{OH})_3 \text{ sludge produced} &= \left[\frac{2(78 \text{ g} / \text{mole})}{(666.5 \text{ g} / \text{mole})} \right] \left[\frac{(12.5 \text{ g} / \text{m}^3)}{(10^3 \text{ g} / \text{kg})} \right] \\ &= 2.9 \text{ kg} / 10^3 \text{ m}^3 \end{aligned}$$

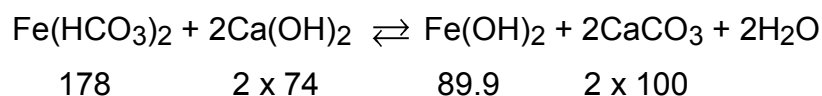
Solution – Part b

1. Determine the amount of $\text{Fe}(\text{HCO}_3)_2$ formed using Eq. (6-12) assuming a dose of 50 kg/4000 m^3 ($= 12.5 \text{ kg} / 10^3 \text{ m}^3$) of ferrous sulfate and lime



$$\text{Fe}(\text{HCO}_3)_2 \text{ produced} = \frac{(178 \text{ g} / \text{mole})}{(278 \text{ g} / \text{mole})} \times \frac{(12.5 \text{ g} / \text{m}^3)}{(10^3 \text{ g} / \text{kg})} = 8.0 \text{ kg} / 10^3 \text{ m}^3$$

2. Determine the amount of CaCO_3 and $\text{Fe}(\text{OH})_2$ formed using Eq. (6-14).



$$\text{CaCO}_3 \text{ produced} = \frac{2(100 \text{ g} / \text{mole})(8.0 \text{ kg} / 10^3 \text{ m}^3)}{(178 \text{ g} / \text{mole})} = 9.0 \text{ kg} / 10^3 \text{ m}^3$$

$$\text{Fe}(\text{OH})_2 \text{ formed} = \frac{(89.9 \text{ g} / \text{mole})(8.0 \text{ kg} / 10^3 \text{ m}^3)}{(178 \text{ g} / \text{mole})} = 4.1 \text{ kg} / 10^3 \text{ m}^3$$

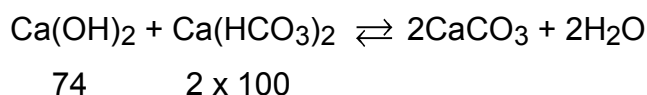
3. Determine the amount of lime $[\text{Ca}(\text{OH})_2]$ consumed in the reaction with $\text{Fe}(\text{HCO}_3)_2$.

$$\text{Lime used} = \frac{2(74 \text{ g / mole})(8.0 \text{ kg} / 10^3 \text{ m}^3)}{(178 \text{ g / mole})} = 6.7 \text{ kg} / 10^3 \text{ m}^3$$

4. Determine the amount of lime remaining.

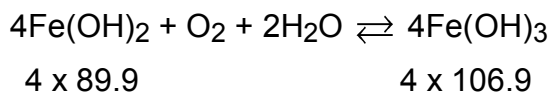
$$\text{Lime remaining} = (12.5 - 6.7) \text{ kg} / 10^3 \text{ m}^3 = 5.8 \text{ kg} / 10^3 \text{ m}^3$$

5. Using Eq. (6-11) determine the amount of CaCO_3 formed when the remaining lime reacts with the alkalinity.



$$\text{CaCO}_3 \text{ produced} = \frac{2(100 \text{ g / mole})(5.8 \text{ kg} / 10^3 \text{ m}^3)}{(74 \text{ g / mole})} = 15.7 \text{ kg} / 10^3 \text{ m}^3$$

6. Determine the amount of $\text{Fe}(\text{OH})_3$ formed using Eq. (6-15).



$$\text{Fe}(\text{OH})_3 \text{ formed} = \frac{4(106.9 \text{ g / mole})(4.1 \text{ kg} / 10^3 \text{ m}^3)}{4(89.9 \text{ g / mole})} = 4.9 \text{ kg} / 10^3 \text{ m}^3$$

7. Determine the total amount of sludge produced.

Sludge produced =

$$= \underset{\text{step 6}}{\text{Fe}(\text{OH})_3} + \underset{\text{step 2}}{\text{CaCO}_3} + \underset{\text{step 5}}{\text{CaCO}_3} - 15 \text{ kg} / 10^3 \text{ m}^3 \text{ dissolved CaCO}_3$$

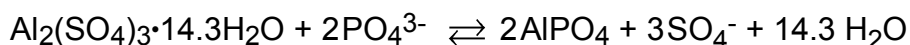
$$\text{Sludge produced} = (4.9 + 9.0 + 15.7 - 15) \text{ kg} / 10^3 \text{ m}^3 = 14.6 \text{ kg} / 10^3 \text{ m}^3$$

PROBLEM 6-4

Problem Statement - See text, page 544-545

Solution – Part a

1. Determine the amount of AlPO_4 formed, and the amount of alum which reacts to form AlPO_4 using Eq. (6-19).



$$599.7 \quad 2 \times 31 \text{ as P} \quad 2 \times 122$$

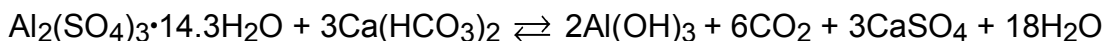
$$\text{AlPO}_4 \text{ formed} = \frac{2(122 \text{ g / mole})(10 \text{ kg} / 10^3 \text{ m}^3)}{2(31.0 \text{ g / mole})} = 39.5 \text{ kg} / 10^3 \text{ m}^3$$

Amount of alum reacting with P

$$\text{Alum reacting with P} = \frac{(599.7 \text{ g / mole})(10 \text{ kg} / 10^3 \text{ m}^3)}{2(31.0 \text{ g / mole})} = 96.7 \text{ kg} / 10^3 \text{ m}^3$$

- Determine the amount of alum which reacts with alkalinity to form $\text{Al}(\text{OH})_3$ and the amount of $\text{Al}(\text{OH})_3$ formed using Eq. (6-9). Assume an alum dosage of 150 g/m^3

$$\text{Amount of alum remaining} = (150 - 96.7) \text{ g/m}^3 = 53.3 \text{ g/m}^3$$



$$599.7 \quad 3 \times 100 \text{ as CaCO}_3 \quad 2 \times 78$$

$$\text{Al}(\text{OH})_3 \text{ formed} = \frac{2(78 \text{ g / mole})(53.3 \text{ kg} / 10^3 \text{ m}^3)}{(599.7 \text{ g / mole})} = 13.9 \text{ kg} / 10^3 \text{ m}^3$$

- Determine the amount of sludge produced.

$$\text{Sludge produced} = [\text{AlPO}_4 + \text{Al}(\text{OH})_3 + 0.95 \times \text{TSS}] Q$$

$$Q = (0.75 \text{ m}^3/\text{s} \times 86,400 \text{ s/d}) = 64.8 \times 10^3 \text{ m}^3/\text{d}$$

$$\text{Sludge produced} =$$

$$= (39.5 + 13.9 + 0.95 \times 220) \text{ g/m}^3 (64.8 \times 10^3 \text{ m}^3/\text{d}) / (10^3 \text{ g/kg})$$

$$= 17,004 \text{ kg/d}$$

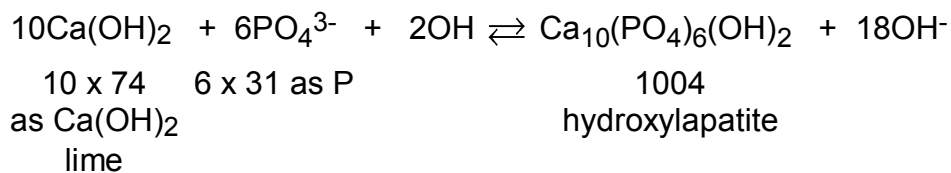
If sludge has a specific gravity of 1.04 and a water content of 93%, then the

Volume of sludge produced

$$\text{Sludge volume} = \frac{(17,004 \text{ kg / d})}{(0.07)(1.04)(10^3 \text{ kg / m}^3)} = 233.6 \text{ m}^3 / \text{d}$$

Solution – Part b

- Determine the amount of hydroxylapatite formed, the amount of lime which reacts with the phosphorus and the amount of lime remaining after the precipitation of phosphorus. The amount of hydroxylapatite formed can be determined using Eq. (6-22).



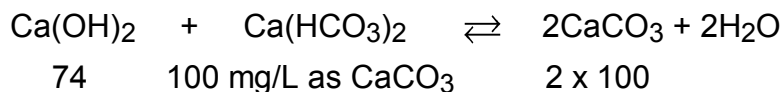
$$\text{Hydroxylapatite formed} = \frac{(1004 \text{ g/mole})(10 \text{ kg}/10^3 \text{ m}^3)}{6(31 \text{ g/mole})} = 54.0 \text{ kg}/10^3 \text{ m}^3$$

$$\text{Lime reacting with P} = \frac{10(74 \text{ g/mole})(10 \text{ kg}/10^3 \text{ m}^3)}{6(31 \text{ g/mole})} = 39.8 \text{ kg}/10^3 \text{ m}^3$$

$$\text{Lime remaining} + (450 - 39.8) \text{ kg}/10^3 \text{ m}^3 = 410.2 \text{ kg}/10^3 \text{ m}^3$$

2. Determine the amount of lime $[\text{Ca(OH)}_2]$ which reacts with alkalinity to form CaCO_3 and the amount of CaCO_3 which precipitates.

The amount of alkalinity present is $200 \text{ g}/\text{m}^3$ as CaCO_3 .



$$\text{CaCO}_3 \text{ formed} = \frac{2(100 \text{ g/mole})(200 \text{ kg}/10^3 \text{ m}^3)}{(100 \text{ g/mole})} = 400 \text{ kg}/10^3 \text{ m}^3$$

$$\text{Amount of CaCO}_3 \text{ that precipitates} = (400 - 20) \text{ kg}/10^3 \text{ m}^3 = 380 \text{ kg}/10^3 \text{ m}^3$$

3. Determine the amount of Ca(OH)_2 that remains in solution. The amount of Ca(OH)_2 that reacts with alkalinity is:

$$\text{Ca(OH)}_2 \text{ utilized} = \frac{(74 \text{ g/mole})(200 \text{ kg}/10^3 \text{ m}^3)}{(100 \text{ g/mole})} = 148.0 \text{ kg}/10^3 \text{ m}^3$$

Amount of Ca(OH)_2 that remains in solution =:

$$= (410.2 - 148.0) \text{ kg}/10^3 \text{ m}^3 = 262.2 \text{ kg}/10^3 \text{ m}^3$$

4. Determine the amount of sludge produced.

$$\text{Sludge produced} = [\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + \text{CaCO}_3 + 0.95 \times \text{TSS}] Q$$

$$\begin{aligned}
 \text{Sludge produced} &= [54.0 + 380 + 0.95 \times 220] \text{ g}/\text{m}^3 (64.8 \times 10^3 \text{ m}^3) / (10^3 \text{ g/kg}) \\
 &= 41,666 \text{ kg/d}
 \end{aligned}$$

If sludge has a specific gravity of 1.05 and a water content of 92%, then the

Volume of sludge produced

$$\text{Sludge volume} = \frac{(41,666 \text{ kg / d})}{(0.08)(1.05)(10^3 \text{ kg / m}^3)} = 496 \text{ m}^3 / \text{d}$$

Solution – Part c

1. Determine the net increase in hardness for the treatment specified in part b.
Assume calcium hardness is equal to the alkalinity

Amount of lime remaining in solution = 262.2 g/m^3 as CaCO_3 (see Part b, Step 3)

Hardness of lime remaining expressed as CaCO_3 =

$$= \frac{(100 \text{ g / mole})(262.2 \text{ g / m}^3)}{(74 \text{ g / mole})} = 354.3 \text{ g / m}^3 \text{ as } \text{CaCO}_3$$

Total hardness remaining = $354.3 + 20 \text{ g/m}^3 = 374.3 \text{ g/m}^3$ as CaCO_3

Net increase in hardness = $(374.3 - 200) \text{ g/m}^3 = 174.3 \text{ g/m}^3$ as CaCO_3

PROBLEM 6-5

Problem Statement - See text, page 545

Instructors Note: The purpose of Problem 6-5 is to introduce students to the computational procedures used to produce graphical solubility diagrams

PROBLEM 6-6

Problem Statement - See text, page 545

Instructors Note: The purpose of Problem 6-6, is to introduce the students to the computational procedures used to produce curves of residual soluble metal concentrations as function of pH.

Sources for chemical equilibrium data are:

Benefield, L. D., J. F. Judkins, Jr., and B. L. Weand (1982) *Process Chemistry for Water and Wastewater Treatment*, Prentice-Hall, Inc., Englewood Cliffs, NJ.

Benjamin, M. M. (2001) *Water Chemistry*, McGraw-Hill, New York

Morel, F. M. M., and J. G. Hering. (199) *Principles and Applications of Aquatic Chemistry*, A Wiley-Interscience publication, New York, NY.

Pankow, J. F. (1991) *Aquatic Chemistry Concepts*, Lewis Publishers, Chelsea, MI.

Sawyer, C. N., P. L. McCarty, and G. F. Parkin (2001) *Chemistry For Environmental Engineering*, 5th ed., McGraw-Hill, Inc., New York, NY.

Snoeyink, V. L., and D. Jenkins (1980) *Water Chemistry*, John Wiley & Sons, New York, NY.

PROBLEM 6-7

Problem Statement - See text, page 545

Instructors Note: The purpose of Problem 6-7, is to introduce the students to the computational procedures used to produce curves of residual soluble metal concentrations as function of pH.

Sources for chemical equilibrium data are:

Benefield, L. D., J. F. Judkins, Jr., and B. L. Weand (1982) *Process Chemistry for Water and Wastewater Treatment*, Prentice-Hall, Inc., Englewood Cliffs, NJ.

Benjamin, M. M. (2001) *Water Chemistry*, McGraw-Hill, New York

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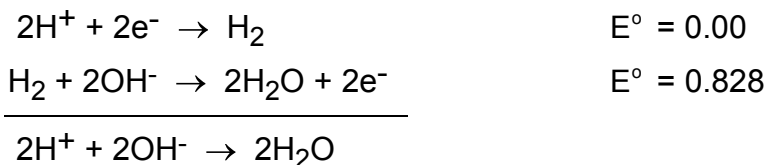
Snoeyink, V. L., and D. Jenkins (1980) *Water Chemistry*, John Wiley & Sons, New York, NY.

PROBLEM 6-8

Problem Statement - See text, page 545

Solution

1. Determine the overall reaction by adding the two half reactions



2. Determine the $E^\circ_{\text{reaction}}$ for overall reaction

$$\begin{aligned}
 E^\circ_{\text{reaction}} &= E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}} \\
 E^\circ_{\text{reaction}} &= (0.828) - (0.00) = +0.828 \text{ volts}
 \end{aligned}$$

3. Determine the equilibrium constant at 25°C using Eq. (6-42)

$$\log K = \frac{n E^\circ_{\text{reaction}}}{0.0592} = \frac{1(0.828)}{0.0592} = 13.99$$

$$K = 10^{13.99}$$

The computed value is the same as the value reported in most texts at 25°C

PROBLEM 6-9

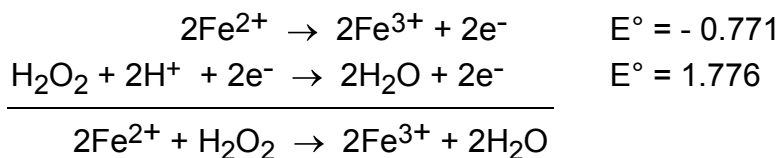
Problem Statement - See text, page 545

Instructors Note:

1. The purpose of Problems 6-9 through 6-12 is to illustrate to students why reactions used commonly in environmental engineering do occur

Solution

1. Determine the overall reaction by adding the two half reactions



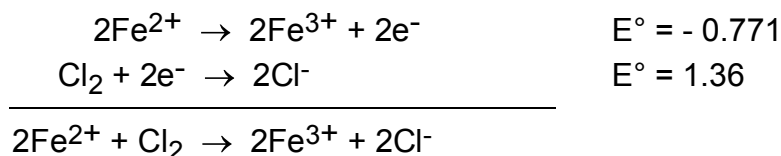
2. Determine the $E^\circ_{\text{reaction}}$ for overall reaction

$$\begin{aligned}
 E^\circ_{\text{reaction}} &= E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}} \\
 E^\circ_{\text{reaction}} &= (1.776) - (-0.771) = +2.547 \text{ volts}
 \end{aligned}$$

Because the $E^\circ_{\text{reaction}}$ for the reaction is positive, the reaction will proceed as written.

PROBLEM 6-10**Problem Statement** - See text, page 545**Solution**

1. Determine the overall reaction by adding the two half reactions



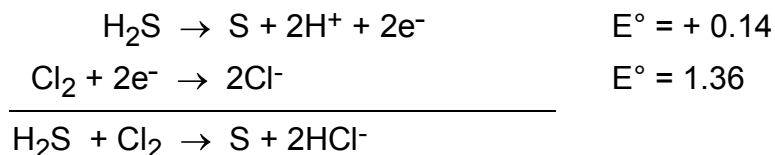
2. Determine the $E^\circ_{\text{reaction}}$ for overall reaction

$$\begin{aligned}
 E^\circ_{\text{reaction}} &= E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}} \\
 E^\circ_{\text{reaction}} &= (1.360) - (-0.771) = +2.131 \text{ volts}
 \end{aligned}$$

Because the $E^\circ_{\text{reaction}}$ for the reaction is positive, the reaction will proceed as written.

PROBLEM 6-11**Problem Statement** - See text, page 545**Solution**

1. Determine the overall reaction by adding the two half reactions



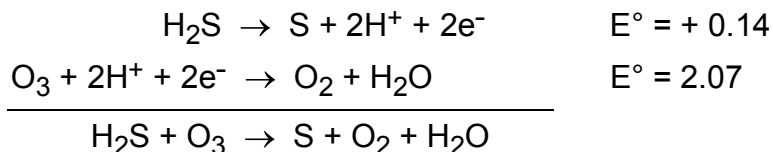
2. Determine the $E^\circ_{\text{reaction}}$ for overall reaction

$$\begin{aligned}
 E^\circ_{\text{reaction}} &= E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}} \\
 E^\circ_{\text{reaction}} &= (1.36) - (0.14) = +1.22 \text{ volts}
 \end{aligned}$$

Because the $E^\circ_{\text{reaction}}$ for the reaction is positive, the reaction will proceed as written.

PROBLEM 6-12**Problem Statement** - See text, page 545**Solution**

1. Determine the overall reaction by adding the two half reactions



2. Determine the $E^\circ_{\text{reaction}}$ for overall reaction

$$E^\circ_{\text{reaction}} = E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}}$$

$$E^\circ_{\text{reaction}} = (2.07) - (0.14) = + 1.93 \text{ volts}$$

Because the $E^\circ_{\text{reaction}}$ for the reaction is positive, the reaction will proceed as written.

PROBLEM 6-13

Problem Statement - See text, page 545

Solution

1. Convert the given data for **Sample 3** for use in determining the Langelier and Ryzner indexes

a.. Given data

Constituent	Unit	Sample 3
Ca^{2+}	mg/L as CaCO_3	245
HCO_3^-	mg/L as CaCO_3	200
TDS	mg/L	600
pH	unitless	6.9

b. Converted data

Constituent	mg/L	mole/L
Ca^{2+}	98.20	2.45×10^{-3}
HCO_3^-	244.0	4.07×10^{-3}

2. Determine the ionic strength of the treated water using Eq. (2-11)

$$I = 2.5 \times 10^{-5} \times \text{TDS}$$

$$I = 2.5 \times 10^{-5} \times 600 \text{ mg/L} = 1.5 \times 10^{-2}$$

3. Determine the activity coefficients for calcium and bicarbonate using Eq. (2-12).

a. For calcium

$$\begin{aligned}\log \gamma_{\text{Ca}^{2+}} &= -0.5 (Z_i)^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right) \\ &= -0.5 (2)^2 \left[\frac{\sqrt{1.5 \times 10^{-2}}}{1 + \sqrt{1.5 \times 10^{-2}}} - 0.3 (1.5 \times 10^{-2}) \right] \\ &= -0.2092\end{aligned}$$

$$\gamma_{\text{Ca}^{2+}} = 0.6177$$

b. For bicarbonate

$$\begin{aligned}\log \gamma_{\text{HCO}_3^-} &= -0.5 (Z_i)^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right) \\ &= -0.5 (1)^2 \left[\frac{\sqrt{1.5 \times 10^{-2}}}{1 + \sqrt{1.5 \times 10^{-2}}} - 0.3 (1.5 \times 10^{-2}) \right] \\ &= -0.0523\end{aligned}$$

$$\gamma_{\text{HCO}_3^-} = 0.8865$$

4. Determine the saturation pH_s at 20°C using Eq. (6-73).

$$\begin{aligned}\text{pH}_s &= -\log \left(\frac{K_{a2} \gamma_{\text{Ca}^{2+}} [\text{Ca}^{2+}] \gamma_{\text{HCO}_3^-} [\text{HCO}_3^-]}{K_{\text{sp}}} \right) \\ \text{pH}_s &= -\log \left[\frac{(4.17 \times 10^{-11})(0.6177)(2.45 \times 10^{-3})(0.8865)(4.07 \times 10^{-3})}{5.25 \times 10^{-9}} \right] \\ \text{pH}_s &= -\log(4.89 \times 10^{-8}) = 7.31\end{aligned}$$

5. Determine the Langelier and Ryzner indexes using Eqs. (6-71) and (6-72)

a. Langelier Saturation Index

$$\text{LSI} = \text{pH} - \text{pH}_s = 6.9 - 7.31 = -0.41$$

$\text{LSI} < 0$ (Water is undersaturated with respect to calcium carbonate)

b. Ryzner Stability Index

$$\text{RSI} = 2\text{pH}_s - \text{pH} = 2(7.31) - 6.9 = 7.72$$

$6.8 < (\text{RSI} = 7.72) < 8.5$ (Water is aggressive)

Comment

Although both indexes are used, the Langelier Saturation Index is used most commonly in the water and wastewater field while the Ryzner Stability Index is used most commonly in industrial applications.

PROBLEM 6-14

Problem Statement - See text, page 545

Solution

1. Determine the ionic strength of **Sample 1** using Eq. (2-10)
 - a. Prepare a computation table to determine the summation term in Eq. (2-10).

Ion	Conc., C, mg/L	C x 10 ³ , mole/L	Z ²	CZ ² x 10 ³
Ca ²⁺	121.3	3.026	4	12.104
Mg ²⁺	36.2	1.489	4	5.956
Na ⁺	8.1	0.352	1	0.352
K ⁺	12	0.307	1	0.307
HCO ₃ ⁻	280	4.590	1	4.590
SO ₄ ²⁻	116	1.208	4	4.832
Cl ⁻	61	1.721	1	1.721
NO ₃ ⁻	15.6	0.252	1	0.252
Sum				30.114

- b. Determine the ionic strength for the concentration C

$$I = \frac{1}{2} \sum C_i Z_i^2 = \frac{1}{2} (30.114 \times 10^{-3}) = 15.057 \times 10^{-3}$$

2. Determine the activity coefficients for the monovalent and divalent ions using Eq. (2-12).
 - a. For monovalent ions

$$\begin{aligned}\log \gamma &= -0.5(Z_i)^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right) \\ &= -0.5(1)^2 \left[\frac{\sqrt{15.057 \times 10^{-3}}}{1 + \sqrt{15.057 \times 10^{-3}}} - 0.3(15.057 \times 10^{-3}) \right] \\ &= -0.0524\end{aligned}$$

$$\gamma = 0.8864$$

b. For divalent ions

$$\begin{aligned}\log \gamma &= -0.5(Z_i)^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right) \\ &= -0.5(2)^2 \left[\frac{\sqrt{15.057 \times 10^{-3}}}{1 + \sqrt{15.057 \times 10^{-3}}} - 0.3(15.057 \times 10^{-3}) \right] \\ &= -0.2096\end{aligned}$$

$$\gamma = 0.6172$$

3. Determine the saturation pH_s at 20°C using Eq. (6-73).

$$\begin{aligned}\text{pH}_s &= -\log \left(\frac{K_{a2} \gamma_{\text{Ca}^{2+}} [\text{Ca}^{2+}] \gamma_{\text{HCO}_3^-} [\text{HCO}_3^-]}{K_{\text{sp}}} \right) \\ \text{pH}_s &= -\log \left[\frac{(4.17 \times 10^{-11})(0.8864)(3.026 \times 10^{-3})(0.6172)(4.590 \times 10^{-3})}{5.25 \times 10^{-9}} \right] \\ \text{pH}_s &= -\log (6.80 \times 10^{-8}) = 7.17\end{aligned}$$

4. Determine the Langelier and Ryzner indexes

a. Langelier Saturation Index

$$\text{LSI} = \text{pH} - \text{pH}_s = 7.2 - 7.17 = -0.0327$$

$\text{LSI} \approx 0$ Water is essentially neutral (i.e., neither scale forming or scale removing with respect to calcium carbonate)

b. Ryzner Stability Index

$$\text{RSI} = 2\text{pH}_s - \text{pH} = 2(7.17) - 7.2 = 7.13$$

$6.8 < (\text{RSI} = 7.13) < 8.5$ (Water is aggressive)

Comment

Although both indexes are used, the Langelier index is used most commonly in the water and wastewater field while the Ryzner index is used most commonly in industrial applications.

PROBLEM 6-15

Problem Statement - See text, page 546

Solution

1. Langelier Saturation Index

$$LSI = pH - pH_s$$

The Langelier Saturation Index was developed from a consideration of carbonate equilibrium (i.e., the effect of pH on the precipitation of calcium carbonate). The pH value at which CaCO_3 will neither be deposited or dissolved is defined as the pH_s value. Thus, if the LSI value is positive, the water is supersaturated with respect to CaCO_3 and scale formation may occur. Similarly if the LSI value is negative, the water is undersaturated and existing to CaCO_3 coatings may be dissolved.

2. Ryzner Stability Index

$$RSI = 2pH_s - pH$$

The Ryzner Stability Index was developed from empirical observations of the dissolution or formation of film in heated water pipes and glass coils.

3. An excellent discussion of the relative merits of the two indexes may be found in:

Schock, M R. (1999) Chapter 17: "Internal Corrosion and Deposition Control," in R. D. Letterman, ed., *Water Quality And Treatment: A Handbook of Community Water Supplies*, 5th ed., American Water Works Association, McGraw-Hill, New York, NY.

PROBLEM 6-16

Problem Statement - See text, page 546

Instructors Note: Students will need to research and find, or be provided with the required molecular weight and hydroxyl radical rate constant for the compound of interest. If desired, the compounds and concentrations may be varied to demonstrate processes that may not be feasible due to insufficient concentrations of HO• (i.e., concentrations which fall outside of the range that can be transferred to water).

Solution

1. Develop a relationship to find the required reaction rate for the given reaction time. A sample computation for chlorobenzene is shown below.

$$r_R = \frac{\text{moles of R lost or gained due to reaction}}{\text{volume} \times \text{time}}$$

$$r_R = \frac{(0.095 \text{ mg/L}) / (112560 \text{ mg/mole})}{10 \text{ s}} = 8.44 \times 10^{-8} \text{ mole/L} \cdot \text{s}$$

2. Rearrange Eq. (6-57) to solve for the hydroxyl radical concentration required to carry out the reaction.

$$C_{\text{HO}\cdot} = \frac{r_R}{k_R C_R} = \frac{(8.44 \times 10^{-8} \text{ mole/L} \cdot \text{s})}{(4.5 \times 10^9 \text{ L/mole} \cdot \text{s})(8.88 \times 10^{-7} \text{ mole/L})} \\ = 2.1 \times 10^{-11} \text{ mole/L}$$

3. Evaluate the feasibility of the reaction.

Because the required hydroxyl radical concentration is within the range attainable using current technology (e.g., 10^9 to 10^{11}), the process is considered to be feasible. A summary table of hydroxyl radical concentrations for other compounds given in the problem statement are given below. As stated, all of the processes are considered feasible, however, interferences and other non-idealities may inhibit a given process. Pilot testing is recommended to evaluate an AOP process for a given water.

Compound	Molecular	Rate constant,	HO• concentration, mole/L
----------	-----------	----------------	---------------------------

	weight, g/mole	L/mole•s	Water A	Water B
Chlorobenzene	112.56	4.50E+09	2.1E-11	2.1E-11
Chloroethene	62.498	1.20E+10	7.9E-12	8.1E-12
TCE	131.39	4.20E+09	2.3E-11	2.2E-11
Toluene	92.14	3.00E+09	3.2E-11	3.1E-11

PROBLEM 6-17**Problem Statement** - See text, page 546

Instructors Note: Students should be assigned a constituent from Table 6-17 for purposes of solving the problem.

Solution

- Develop an expression for the concentration of the constituent as a function of time in a completely mixed batch reactor (CMBR). Note that the residence time for an ideal plug flow reactor is equivalent to the residence time in a completely mixed batch reactor. The required computation for chlorobenzene is given below.

- Using Eq. (6-58), the rate expression for a CMBR, where C_R represents the concentration of the selected constituent is given by

$$r_R = \frac{dC_R}{dt} = -k_R C_{HO} \cdot C_R = -k' C_R$$

$$\text{where } k' = k_R C_{HO}.$$

- The integrated form of the rate expression for a CMBR is:

$$\int_{C_{R0}}^{C_R} \frac{dC_R}{C_R} = -\int_0^t k' dt$$

$$C_R = C_{R0} e^{-k' t}$$

- Calculate the time it would take to achieve a concentration of 1.25 $\mu\text{g/L}$ ($25 \mu\text{g/L} \times 0.05$) using the equation developed in step 1.

- a. Rearrange the above equation to solve for t.

$$t = \frac{1}{k'} \ln \frac{C_{R0}}{C_R}$$

- b. Solve for the reaction time. The reaction time is given below for several hydroxyl radical concentrations that may be attained using different reactor designs.

Using the value of k' from step 1 and an $\text{HO}\cdot$ concentration of 10^{-9} mole/L, the reaction time is calculated for the selected constituent (**chloride ion**):

$$k' = k_R C_{\text{HO}\cdot} = (4.30 \times 10^9 \text{ L / mole}\cdot\text{s})(10^{-9} \text{ mole / L}) = 4.3 \text{ 1/s}$$

$$t = \frac{1}{(4.3)} \ln \left(\frac{25}{1.25} \right) = 0.70 \text{ s}$$

For an $\text{HO}\cdot$ concentration of 10^{-10} mole/L, the reaction time is

$$k' = k_R C_{\text{HO}\cdot} = (4.3 \times 10^9 \text{ L / mole}\cdot\text{s})(10^{-10} \text{ mole / L}) = 0.43 \text{ 1/s}$$

$$t = \frac{1}{(0.43)} \ln \left(\frac{25}{1.25} \right) = 7.0 \text{ s}$$

For an $\text{HO}\cdot$ concentration of 10^{-11} mole/L, the reaction time is

$$k' = k_R C_{\text{HO}\cdot} = (4.3 \times 10^9 \text{ L / mole}\cdot\text{s})(10^{-11} \text{ mole / L}) = 0.043 \text{ 1/s}$$

$$t = \frac{1}{(0.043)} \ln \left(\frac{25}{1.25} \right) = 70 \text{ s}$$

3. Size the reactor for a flowrate of $3800 \text{ m}^3/\text{d}$.
- a. For the $\text{HO}\cdot$ concentration of 10^{-9} mole/L, the reactor size (assuming ideal hydraulics) would be

$$V = Q \cdot t = \frac{(3800 \text{ m}^3 / \text{d})}{(86400 \text{ s / d})} (0.70 \text{ s}) = 0.03 \text{ m}^3 \text{ or } 30 \text{ L}$$

- b. For the $\text{HO}\cdot$ concentration of 10^{-10} mole/L, the reactor size would be

$$V = Q \cdot t = \frac{(3800 \text{ m}^3 / \text{d})}{(86400 \text{ s} / \text{d})} (7.0 \text{ s}) = 0.3 \text{ m}^3 \text{ or } 300 \text{ L}$$

- c. For the $\text{HO}\cdot$ concentration of 10^{-11} mole/L, the reactor size would be

$$V = Q \cdot t = \frac{(3800 \text{ m}^3 / \text{d})}{(86400 \text{ s} / \text{d})} (70 \text{ s}) = 3 \text{ m}^3 \text{ or } 3000 \text{ L}$$

PROBLEM 6-18

Problem Statement - See text, page 546

Solution

1. Calculate the photonic energy input per unit volume of the reactor.

- a. Calculate the total lamp power:

$$P = (25 \text{ lamps} \times 500 \text{ W/lamp}) = 12,500 \text{ W} = 12,500 \text{ J/s}$$

- b. Calculate the photonic energy input for the reactor using Eq. (6-63)

$$P_R = \frac{(12,500 \text{ J/s})(0.3)(254 \times 10^{-9} \text{ m})}{(6.023 \times 10^{23} \text{ 1/einstein})(6.62 \times 10^{-34} \text{ J}\cdot\text{s})(3.0 \times 10^8 \text{ m/s})(250 \text{ L})}$$

$$= 3.185 \times 10^{-5} \text{ einstein/L}\cdot\text{s}$$

2. Calculate the rate constant for NDMA.

- a. The extinction coefficient of NDMA at 254 nm can be obtained from Table 6-18

$$\varepsilon(254) = 1974 \text{ L/mole}\cdot\text{cm}$$

$$\varepsilon'(254) = 2.303 \varepsilon(254) = 2.303 \times 1974 = 4546 \text{ L/mole}\cdot\text{cm}$$

- b. The quantum yield for NDMA can be obtained from Table 6-18.

$$\phi(\lambda)_{\text{NDMA}} = 0.3 \text{ mole/einstein}$$

- c. Compute k_{NDMA} using Eq. (6-66).

$$\begin{aligned}
 k_{\text{NDMA}} &= \phi(\lambda)_{\text{NDMA}} P_R \frac{\varepsilon'(\lambda)_{\text{NDMA}}}{k'(\lambda)} \\
 &= (0.3 \text{ mole / einstein}) (3.185 \times 10^{-5} \text{ einstein / L} \cdot \text{s}) \left[\frac{(4546 \text{ L / mole} \cdot \text{cm})}{(0.01 / \text{cm})} \right] \\
 &= 4.34 \text{ 1/s}
 \end{aligned}$$

3. Calculate the flow rate that can be treated per reactor.

- a. Calculate hydraulic detention time for the reactor.

$$\tau = \frac{n \left[(C_{\text{NDMA},o} / C_{\text{NDMA},e})^{1/n} - 1 \right]}{k_{\text{NDMA}}} = \frac{4 \left[(100 / 10)^{1/4} - 1 \right]}{4.34 \text{ 1/s}} = 0.717 \text{ s}$$

- b. Calculate the flow rate that can be processed by one reactor.

$$Q = \frac{V}{\tau} = \frac{250 \text{ L}}{0.717 \text{ s}} = 349 \text{ L / s}$$

4. Determine the number of reactors needed to treat the full flow.

- The total flow to be treated is $1 \times 10^5 \text{ m}^3/\text{d} = 1157 \text{ L/s}$
- The number of reactors needed is $(1157 \text{ L/s}) / (349 \text{ L/s}) = 3.3$ (use 4)
- The actual number of reactors needed will be greater than the computed value to compensate for lamp failure, fouling, and so that one or more reactors can be taken off line for lamp maintenance without interrupting the flow. It should be noted that the extra reactors will not be in continuous operation, but will only be used when needed or in a service rotation to reduce costs.

5. Calculate the EE/O for the photolysis process.

$$\begin{aligned}
 EE/O &= \frac{P}{Q \log\left(\frac{C_i}{C_f}\right)} \\
 &= \frac{(12.5 \text{ kW})(10^3 \text{ L/m}^3)}{(349 \text{ L/s}) \left[\log\left(\frac{100 \text{ ng/L}}{10 \text{ ng/L}}\right) \right] (3600 \text{ s/h})} = 0.01 \text{ kWh/m}^3
 \end{aligned}$$

The computed EE/O value is low compared to the typical range for ground and surface waters because of the high quality effluent from the RO process. Reverse osmosis removes or reduces many of the constituents that would interfere with photolysis of specific constituents and can produce effluent with low absorbance, improving the efficiency of the photolysis process.

6. Estimate the overall daily energy usage for the process.

For the two operational reactors, the estimated energy usage is

$$(4 \text{ reactors})(12.5 \text{ kW})(24 \text{ h/d}) = 1200 \text{ kWh/d}$$

7. Prepare a summary table of results for various absorptivity values.

As shown in the following table, absorptivity has a significant effect on the number of reactors and energy required for photolysis.

Absorptivity, cm^{-1}	$K_{\text{NDMA}},$ 1/s	$Q_{\text{Reactor}},$ L/s	Number of reactors (rounded up)	EE/O, kWh/m^3	Energy usage, kWh/d
0.01	4.34	349	4	0.01	1200
0.05	0.869	70	17	0.05	5100
0.1	0.434	35	34	0.1	10,200

PROBLEM 6-19

Problem Statement - See text, page 546

Instructors Note: Students will need to make assumptions about the process, including the absorptivity coefficient and reactor characteristics. Thus, responses

will be dependant on the various assumptions made and degree of process optimization.

Solution

1. Calculate the amount of energy required using the procedure outlined in Example 6-8. Assuming that three reactors (as described in Example 6-8) are needed to accomplish the required treatment, the resulting EE/O value is computed as follows:

$$Q = \frac{V}{\tau} = \frac{242 \text{ L}}{4.22 \text{ s}} = 57.4 \text{ L/s}$$

$$EE/O = \frac{P}{Q \log\left(\frac{C_i}{C_f}\right)} = \frac{(14.4 \text{ kW})(10^3 \text{ L/m}^3)}{(57.4 \text{ L/s}) \left\{ \log \left[\frac{(100 \text{ ng/L})}{(1 \text{ ng/L})} \right] \right\} (3600 \text{ s/h})} = 0.035 \text{ kWh/m}^3$$

Using an electricity cost of \$0.13/kWh, the cost is computed as follows.

$$(\$0.13/\text{kWh})(0.035 \text{ kWh/m}^3)(3800 \text{ m}^3/\text{d}) = \$17.22/\text{d}$$

PROBLEM 6-20

Problem Statement - See text, page 546

Solution

1. Prepare a table to summarize the chemical properties of importance for determining the advanced treatment process that should be considered. For some of the compounds to be investigated, Table 16-12, page 1769, may be used to find chemical properties, other compounds will require review of other literature references.

Compound	Formula	mw	H, m ³ -atm/mole	Solubility, mg/L
Benzene	C ₆ H ₆	78.1	5.5 E-3	1,780
Chloroform	CHCl ₃	119.4	3.1 E-3	7,840

Dieldrin	$C_{12}H_8Cl_6O$	380.9	1.0 E-5	0.195
Heptachlor	$C_{10}H_5Cl_7$	373.3	2.9 E-4	0.18
N-Nitrosodi- methylamine	$C_2H_6N_2O$	74.1	2.63 E-7	1,000,000
Trichloroethylene	C_2HCl_3	131.4	9.9 E-3	1,280
Vinyl chloride	C_2H_3Cl	62.5	2.8 E-2	8,800

2. Prepare a table to summarize the compounds and the treatment processes that are expected to be effective for removal of that compound. The information in Table 6-1 may be useful as a guide in process selection.

Compound	Advanced treatment processes for removal of specified compound ^a
Benzene	Advanced oxidation, ozonation
Chloroform	Advanced oxidation
Dieldrin	Advanced oxidation
Heptachlor	Advanced oxidation
N-Nitrosodi- methylamine	Advanced oxidation, photolysis
Trichloroethylene	Advanced oxidation
Vinyl chloride	Advanced oxidation

^a Descriptions of the various processes are presented in the following table

Note: The problem statement as written refers to treatment methods discussed in Chap. 6 only (e.g., advanced oxidation, chemical oxidation, chemical coagulation, and chemical precipitation). An identical question is provided in Chap. 11 for separation processes (i.e., filtration processes, reverse osmosis, electrodialysis, ion exchange and adsorption).

Advanced treatment process discussed in Chap. 6 and their applications.

Advanced treatment process	Typical applications
Conventional chemical oxidation	Removal of trace organic compounds using ozone (O_3)
Advanced oxidation	Removal of dissolved organic compounds using hydroxyl radicals for oxidation.
Photolysis	Removal of trace organic constituents using exposure to UV light