

## Lecture 24

# OXIDATION AND PHOTOLYSIS (2)

Course: Water Reuse  
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## AOP design

- Commercially available AOPs are rated for a given hydroxyl radical output. Reported field HO $\cdot$  concentrations range from  $10^{-11}$  to  $10^{-9}$  moles/L
- The reactions are second order because they depend on the concentration of the hydroxyl radical and the compound undergoing oxidation. The second order rate law,  $r_R$  is given by the following expression:

$$r_R = -k_R C_{HO\cdot} C_R$$

$r_R$  = second order rate law, mole/L $\cdot$ s  
 $k_R$  = second order rate constant for the destruction of R with HO $\cdot$  radicals, mole/L $\cdot$ s  
 $C_{HO\cdot}$  = concentration of hydroxyl radical, mole/L  
 $C_R$  = concentration of the target organic R, mole/L

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## AOP design

The half-life of the target organic compounds may be calculated assuming that the HO $\cdot$  is constant and equal to a typical field value or manufacturers specification. The expression for the half-life of an organic compound is obtained by substituting the rate law into a mass balance on a batch reactor whose contents are mixed completely, and solving and rearranging the result, as follows:

$$\frac{dC_R}{dt} = -k_R C_{HO\cdot} C_R \quad (10-32)$$

$$t_{1/2} = \frac{\ln(2)}{k_R C_{HO\cdot}} \quad (10-33)$$

where  $t_{1/2}$  = the half life of the organic compound R, s

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Compound name	HO $\cdot$ rate constant, L/mole $\cdot$ s	Compound name	HO $\cdot$ rate constant, L/mole $\cdot$ s
Ammonia	$9.00 \times 10^7$	Hypobromous acid	$2.0 \times 10^9$
Arsenic trioxide	$1.0 \times 10^9$	Hypoiodous acid	$5.6 \times 10^4$
Bromide ion	$1.10 \times 10^{10}$	Iodide ion	$1.10 \times 10^{10}$
Carbon tetrachloride	$2.0 \times 10^6$	Iodine	$1.10 \times 10^{10}$
Chlorate ion	$1.00 \times 10^6$	Iron	$3.2 \times 10^8$
Chloride ion	$4.30 \times 10^9$	Methyl tertiary butyl ether (MTBE)	$1.6 \times 10^9$
Chloroform	$5 \times 10^6$	Nitrite ion	$1.10 \times 10^{10}$
CN $^-$	$7.6 \times 10^9$	N-Dimethylnitrosamine (NDMA)	$4 \times 10^8$
CO $_3^{2-}$	$3.9 \times 10^8$	Ozone	$1.1 \times 10^8$
Dibromochloropropane	$1.5 \times 10^8$	p-Dioxane	$2.8 \times 10^9$
1, 1-Dichloroethane	$1.8 \times 10^8$	Tetrachloroethylene	$2.6 \times 10^9$
1, 2-Dichloroethane	$2.0 \times 10^8$	Tetrachloroethylene	$1.0 \times 10^7$
H $_2$ O $_2$	$2.7 \times 10^7$	Tribromomethane	$1.8 \times 10^8$
HCN	$6.0 \times 10^7$	Trichloroethylene	$4.2 \times 10^9$
HCO $_3^-$	$8.5 \times 10^6$	Trichloromethane	$5.0 \times 10^6$
Hydrogen sulfide	$1.5 \times 10^{10}$	Vinyl chloride	$1.2 \times 10^{10}$

## Example

### EXAMPLE 10-4. Advanced Oxidation Process for Removal of NDMA.

N-nitrosodimethylamine (NDMA) ( $C_2H_6N_2O$ ) is a compound of concern present in many secondary and tertiary treated wastewater effluents. From Table 10-11, the second order rate constant of  $HO\cdot$  for NDMA is  $4 \times 10^8$  L/mole $\cdot$ s. Compute the time required to lower the concentration of NDMA from 200  $\mu$ g/L to 20  $\mu$ g/L for a  $HO\cdot$  concentration of  $10^{-9}$  mole/L using an ideal plug flow reactor. Assume that the residence time for an ideal plug flow reactor is equivalent to the residence time in a completely mixed batch reactor.

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## Solution

### Solution

- Develop an expression of the concentration of NDMA as a function of time in a completely mixed batch reactor (CMBR).
  - Using Eq. (10-32), the rate expression for a CMBR, where  $C_R$  represents the concentration of NDMA is given by:

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

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

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

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

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

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- Calculate the time it would take to achieve a concentration of 20  $\mu$ g/L using the equation developed in Step 1.
  - Rearrange the above equation to solve for t.

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

- Solve for t.

The value of  $k'$  from Step 1 is

$$k' = k_R C_{HO\cdot} = (4 \times 10^8 \text{ L/mole} \cdot \text{s})(10^{-9} \text{ mole/L}) = 0.4 \text{ 1/s}$$

$$t = \frac{1}{(0.4)} \ln \left( \frac{200}{20} \right) = 5.8 \text{ s}$$

### Comment

Advanced oxidation of NDMA appears to be feasible given the short contact time required for the reaction. Because some organic compounds of interest react more slowly with  $HO\cdot$ , these compounds will require longer reaction times and/or high concentrations of  $HO\cdot$ . The presence of background organic matter, carbonate, bicarbonate, and pH will also reduce the efficiency of the AOP and must be considered during process design. As discussed in Chap. 6, pilot testing will be required to determine site specific process design and operational parameters.

## Effect of alkalinity

- High concentrations of carbonate and bicarbonate (known scavengers of  $HO\cdot$  radicals) react with  $HO\cdot$  and reduce the efficiency of AOPs.
- Unfortunately, the concentrations of  $HCO_3^-$  and  $CO_3^{2-}$  are often three orders of magnitude higher than the organic pollutants targeted for destruction.
- Even alkalinities of 50 mg/L reduce the rate by a factor of 10 at a pH of 7. However, at high pH it is even more reduced because the rate constant with  $CO_3^{2-}$  is much larger than  $HCO_3^-$ . To overcome these difficulties, pretreatment is required to remove alkalinity.

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## Other impacts

- Metal ions in reduced oxidation states, such as Fe(II) and Mn(II), can consume a significant quantity of chemical oxidants as well as scavenge HO• radicals.
- Other factors that affect the treatment process include suspended material (which affects light transmission) and the type and nature of the residual TOC and COD.
- HO<sub>2</sub><sup>-</sup> has about 10 times the UV absorbance at 254 nm than does H<sub>2</sub>O<sub>2</sub>; consequently the H<sub>2</sub>O<sub>2</sub>/UV can be more effective at higher pH. Raising the pH to improve the process performance would only be practical if the pH was raised for other purposes such as softening.

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## Photolysis

- Photolysis is a process by which constituents are broken down by exposure and absorption of photons from a light source. In natural systems, sunlight is the light source for photolysis reactions; in engineered systems, UV lamps are used to produce the photonic energy.
- Fouling that may occur on the outside of the UV lamp may be managed using an automatic cleaning system that periodically moves along the lamp to remove precipitates and intercepted matter. Chemicals added to reduce the pH for scale control will also reduce the potential for precipitation on the UV lamps.

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## Beer Lambert law

- The absorbance of a solution is a measure of the amount of light absorbed by constituents in the solution at a specified wavelength and over a fixed path length.

$$A(\lambda) = -\log\left(\frac{I}{I_0}\right) = \epsilon(\lambda) C x = k(\lambda)x \quad (10-35)$$

where  $A(\lambda)$  = absorbance, dimensionless

$I$  = light intensity after passing through solution containing constituents of interest at wavelength,  $\lambda$ , einsteins/cm<sup>2</sup>·s (note: an einstein is equal to one mole of photons)

$I_0$  = light intensity after passing through a blank solution (i.e., distilled water) of known depth (typically 1.0 cm) at wavelength,  $\lambda$ , einstein/cm<sup>2</sup>·s

$\epsilon(\lambda)$  = base 10 extinction coefficient or molar absorptivity of light-absorbing solute at wavelength  $\lambda$ , L/mole·cm

$\lambda$  = wavelength, nm

$C$  = concentration of light absorbing solute, mole/L

$x$  = length of light path, cm

$k(\lambda)$  = absorptivity (base 10), l/cm

## Quantum yields and excitation coefficient

- The excitation coefficient is a function of  $\lambda$  because as the  $\lambda$  decreases more energetic photons are absorbed and the absorptivity of a light-absorbing compound increases.

Compound	Primary quantum yield in aqueous phase, mole/einstein	Extinction coefficient at 253.7 nm, L/mole·cm
NO <sub>3</sub> <sup>-</sup>	—	3.8
HOCl (at 330 nm)	0.23	15
OCl <sup>-</sup>	0.23	190
HOCl	—	53.4
OCl <sup>-</sup>	0.52	155
O <sub>3</sub>	0.5	3300
ClO <sub>2</sub>	0.44	108
Sodium chlorite	0.72	—
TCE	0.54	9
PCE	0.29	205
NDMA	0.3	1974
Water	—	0.0000061

**EXAMPLE 10-5. UV Absorbance by NDMA.**

The chemical compound NDMA (see Chap. 3) is commonly found at low concentrations in reclaimed water, even after treatment by RO. Estimate the absorptivity of NDMA ( $C_2H_6N_2O$ ) at a wavelength of 254 nm, assuming NDMA is present at a concentration of 30 ng/L.

**Solution**

1. Convert the mass concentration of NDMA in solution to mole/L.

Using the periodic table from the back inside cover of this textbook, the molecular weight of NDMA is 74.09 g/mole. The concentration is determined as follows:

$$C = \frac{(30 \text{ ng/L})}{(74.09 \text{ g/mole})} (1 \text{ g}/10^9 \text{ ng}) = 4.05 \times 10^{-10} \text{ mole/L}$$

2. Compute the absorptivity of NDMA using Eq. (10-35).
  - a. Determine the extinction coefficient,  $\epsilon(\lambda)$ , of NDMA from Table 10-12. The extinction coefficient of NDMA at a wavelength of 254 nm is 1974 L/mole-cm.
  - b. The absorptivity,  $k(\lambda)$ , of NDMA is:

$$k(\lambda) = \epsilon(254)C = (1974 \text{ L/mole} \cdot \text{cm})(4.05 \times 10^{-10} \text{ mole/L}) = 8.0 \times 10^{-7} \text{ cm}^{-1}$$

**Several absorbing compounds**

$$\ln\left(\frac{I}{I_0}\right) = -\left[\sum \epsilon'(\lambda)_i C_i\right] x \quad (10-36)$$

$\epsilon'(\lambda)_i$  = extinction coefficient of compound i at wavelength  $\lambda$  (base e), L/(mole·cm);  
note  $\epsilon'(\lambda)_i = 2.303 \epsilon(\lambda)_i$ ;

$C_i$  = concentration of compound i, mole/L

Other terms as defined previously.

- The above is based on a single incident wavelength, such as with low-pressure UV lamps. Multiple wavelength situations (e.g. medium-pressure UV lamps) can be solved using a similar approach, i.e., summing adsorption of each compound for each wavelength.

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**Theoretical maximum photonic energy**

- The actual performance of a photoreactor is expected to be lower than computed using the following equation due to light being absorbed by the reactor walls or blocked by the precipitate that forms on the lamp sleeve:

$$P_R = \frac{P \times \eta}{N_p \times V \times h\nu}$$

$P_R$  = photonic energy input per unit volume of the reactor, einstein/L·s

$P$  = lamp power, J/s (W)

$\eta$  = output efficiency at the wavelength of interest (as a fraction)

$N_p$  = number photons per mole (as einstein),  $6.023 \times 10^{23}$  1/einstein

$V$  = reactor volume, L

$h$  = Planck's constant,  $6.62 \times 10^{-34}$  J·s

$\nu = \frac{c}{\lambda}$  = frequency of light 1/s

$c$  = the speed of light,  $3.00 \times 10^8$  m/s

$\lambda$  = wavelength of the light, m

**Photon absorption rate**

- The rate at which a compound is photolyzed depends on the rate and frequency of photon absorption. The volumetric photon adsorption rate is:

$$I_V = -\frac{dI}{dx} = \epsilon'(\lambda) \cdot C \cdot I_0 \cdot e^{-\epsilon'(\lambda)Cx} \quad (10-38)$$

where  $I_V$  = rate that photons are absorbed per volume of solution at a particular point, einstein/cm<sup>3</sup>·s

$\epsilon'(\lambda)$  = base e extinction coefficient or molar absorptivity of light absorbing solute at wavelength  $\lambda = 2.303\epsilon(\lambda)$ , L/mole·cm

Other terms as defined previously.

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## Quantum yield

- The quantum yield describes the frequency at which photon absorption results in a photolysis reaction (number of photolysis reactions divided by the number of photons absorbed by the molecule).

$$\phi(\lambda) = \frac{-r_R}{I_v} = \frac{\text{Reaction rate}}{\text{Rate of photon absorption}}$$

$\phi(\lambda)$  = quantum yield at wavelength  $\lambda$ , mol/einstein  
 $r_R$  = photolysis rate, mole/(cm<sup>3</sup>·s)

- It is specific to the type of compound and the wavelength. Generally, the quantum yield increases as wavelength decreases (increasing photonic energy).

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## Rate of photolysis

- Typically, the light absorption by the component that is targeted for removal is minor as compared to the light absorption by the background water matrix.
- The pseudo first order rate law for the photolysis is:

$$r_{\text{avg}} = \left[ \phi(\lambda) P_R \frac{\varepsilon'(\lambda)}{k'(\lambda)} \right] C_i = k C_i \quad (10-40)$$

where  $r_{\text{avg}}$  = overall average photolysis rate of the constituent in the reactor, mole/L·s  
 $k'(\lambda)$  = measured absorptivity of the water matrix at wavelength (base e)  $\lambda$ , 1/cm  
 $k$  = pseudo-first order rate coefficient, 1/s  
 Other terms as defined previously.

- After obtaining the rate law,  $r_{\text{avg}}$  an appropriate reactor model may be used

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## Electrical efficiency

- It is important to compare process efficiency on the basis of electrical usage per amount of compound destruction. One such measure is the electrical efficiency per log order (EE/O) of compound destruction per unit volume of water.
- So the power input can be divided by the EE/O to obtain an estimate of the flow rate that can be treated in a given reaction and achieve one order of magnitude reduction in concentration. Consequently, EE/O is a convenient measure because it can be used to estimate the energy that is required to reduce the contaminant concentration by one order of magnitude.

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## Electrical efficiency

$$EE/O = \frac{P \times t}{V \times \log \left[ \frac{C_i}{C_f} \right]} \quad (\text{for batch systems})$$

$$EE/O = \frac{P}{Q \times \log \left[ \frac{C_i}{C_f} \right]} \quad (\text{for continuous flow systems})$$

EE/O = electrical efficiency per log order reduction, kWh/m<sup>3</sup>.

P = lamp power output, kW

t = irradiation time, h

V = reactor volume, m<sup>3</sup>

C<sub>i</sub> = initial concentration, mg/L

C<sub>f</sub> = final concentration, mg/L

Q = water flowrate, m<sup>3</sup>/h

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## Example

### EXAMPLE 10-6. Design of Direct Photolysis Process for NDMA.

A water reclamation plant produces  $1.9 \times 10^4 \text{ m}^3/\text{d}$  (5 Mgal/d) of RO effluent containing 50 ng/L of NDMA. Determine the number of photolysis reactors needed to reduce the NDMA concentration of the RO effluent to 1 ng/L prior to groundwater injection. The photolysis reactors under evaluation are 0.5 m in diameter and 1.5 m long with an effective water volume of 242 L. Each reactor has 72 lamps rated at 200 W per lamp and an output efficiency of 30 percent at 254 nm. Assume that the hydraulic detention time,  $\tau$ , of the reactor can be described using the tanks in series model,  $\tau = n[(C_e/C_o)^{1/n} - 1]/k$ , where  $k$  is the reaction rate constant and  $n$  is the number of tanks in series. Use three tanks in series and neglect all other losses. The RO water has an absorptivity measured at a wavelength of 254 nm of  $k'(\lambda) = 0.02 \text{ cm}^{-1}$ . Calculate the EE/O and daily energy usage for the photolysis process.

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## Solution

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

- a. Calculate the total lamp power:

$$P = (72 \text{ lamps} \times 200 \text{ W/lamp}) = 14,400 \text{ W} = 14,400 \text{ J/s}$$

- b. Calculate the photonic energy input for the reactor using Eq. (10-37)

$$P_R = \frac{(14,400 \text{ J/s})(0.3)(254 \times 10^{-9} \text{ m})}{(6.023 \times 10^{23} \text{ 1/einstein})(6.62 \times 10^{-34} \text{ J} \cdot \text{s})(3.0 \times 10^8 \text{ m/s})(242 \text{ L})} = 3.80 \times 10^{-5} \text{ einstein/L} \cdot \text{s}$$

2. Calculate the rate constant for NDMA.

- a. The extinction coefficient of NDMA at 254 nm can be obtained from Table 10-12.

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

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

- b. The quantum yield for NDMA can be obtained from Table 10-12.

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

## Solution

- c. Compute  $k_{\text{NDMA}}$  using Eq. (10-40).

$$k_{\text{NDMA}} = \phi(\lambda)_{\text{NDMA}} P_R \frac{\epsilon'(\lambda)_{\text{NDMA}}}{k'(\lambda)}$$

$$= (0.3 \text{ mole/einstein})(3.80 \times 10^{-5} \text{ einstein/L} \cdot \text{s}) \left[ \frac{(4546 \text{ L/mole} \cdot \text{cm})}{(0.01/\text{cm})} \right]$$

$$= 2.59 \text{ 1/s}$$

3. Calculate the flowrate that can be treated per reactor.

- a. Calculate hydraulic detention time for the reactor.

$$\tau = \frac{n[(C_{\text{NDMA},o}/C_{\text{NDMA},e})^{1/n} - 1]}{k_{\text{NDMA}}} = \frac{3[(50/1)^{1/3} - 1]}{(2.59 \text{ 1/s})} = 3.11 \text{ s}$$

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

$$Q = \frac{V}{\tau} = \frac{242 \text{ L}}{3.11 \text{ s}} = 77.7 \text{ L/s}$$

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

- a. The total flow to be treated is  $1.9 \times 10^4 \text{ m}^3/\text{d} = 219 \text{ L/s}$ .

- b. The number of reactors needed is  $(219 \text{ L/s})/(77.7 \text{ L/s}) = 2.8$  (use 3).

- c. The actual number of reactors needed will be greater than the computed value to compensate for lamp failure, fouling, and maintenance; and for peak flow conditions. 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 using Eq. (10-42).

$$\text{EE/O} = \frac{P}{Q \times \log \left[ \frac{C_i}{C_f} \right]} = \frac{14.4 \text{ kW} \times (10^3 \text{ L/m}^3)}{(77.7 \text{ L/s}) \times \left[ \log \left( \frac{50 \text{ ng/L}}{1 \text{ ng/L}} \right) \right] \times (3600 \text{ s/h})} = 0.0303 \text{ kWh/m}^3$$

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.

$$3 \text{ reactors} \times 14.4 \text{ kW} \times 24 \text{ h/d} = 1037 \text{ kWh/d}$$