Chemical characteristics of water II

Organic content

- Contaminated water contains various kinds of organic compounds
  - Proteins, carbohydrates, fats and oils, urea, etc. from food and human wastes
  - Synthetic organic compounds
  - Organics released to waters → consumption of dissolved oxygen by microorganisms → anaerobic (septic) condition → destroy aquatic environment (ex: fish kills), odor problems, production of toxic compounds, etc.
  - Removal of organic compounds is one of the major target for wastewater treatment
- Measurement of organic content as a whole
  - Biochemical oxygen demand (BOD)
  - Chemical oxygen demand (COD)
  - Total organic carbon (TOC)

BOD

- Measurement of dissolved oxygen used by microorganisms in the biochemical oxidation of organic matter

- **BOD test procedure**
  - The water sample is diluted such that the difference between the DO before and after the test can be determined (estimated BOD: 2-6 mg/L)
  - The diluted water sample is inoculated with microorganisms that degrade organic matter
  - The diluted, inoculated water sample is incubated for a certain time period (usually 5 days)
  - The DO before and after the incubation is measured to determine the BOD of the sample

#1

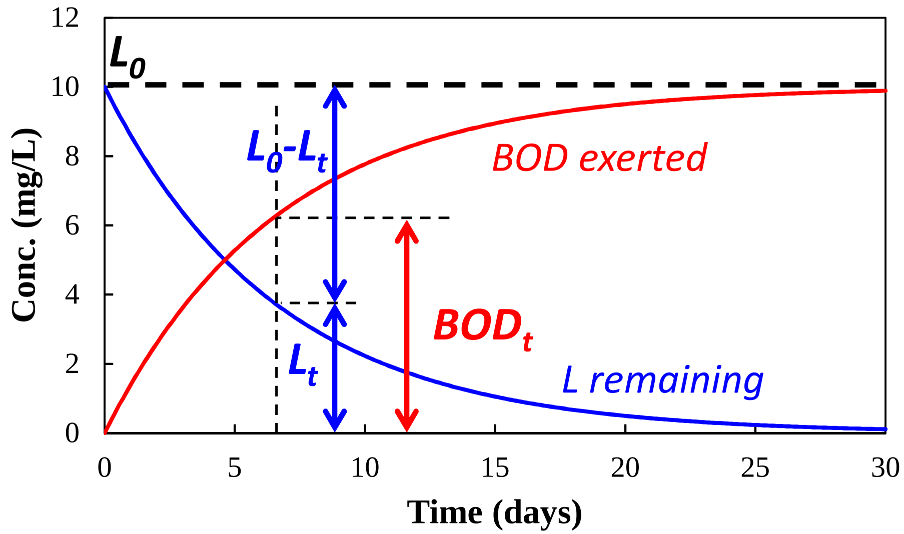
#2

BOD

- Modeling BOD reaction: **assume first-order reaction**

$$\frac{d(L_t)}{dt} = -k_1 L_t$$

L_t = amount of organics remaining at time t (d) expressed in oxygen equivalents (mg O_2/L)
k_1 = first-order rate constant (1/d)



Integrating from *t=0* to *t*,

$$L_t = L_0\left(e^{-k_1 t}\right)$$

Note
$BOD_t = L_0 - L_t$
L_0 = UBOD

UBOD = ultimate BOD (mg/L)

BOD

$$\rightarrow \boxed{BOD_t = UBOD - L_t = UBOD\left(1 - e^{-k_1 t}\right)}$$

BOD_t *= the BOD value at time t (mg/L)*

- Temperature effect
  - modified van't Hoff-Arrhenius relationship:

$$k_{1_T} = k_{1_{20}} \theta^{T-20}$$

T *= temperature in ℃*

  - Typically used value of θ:
    1.056 (20-30°C) / 1.135 (4-20°C)

NBOD vs. CBOD

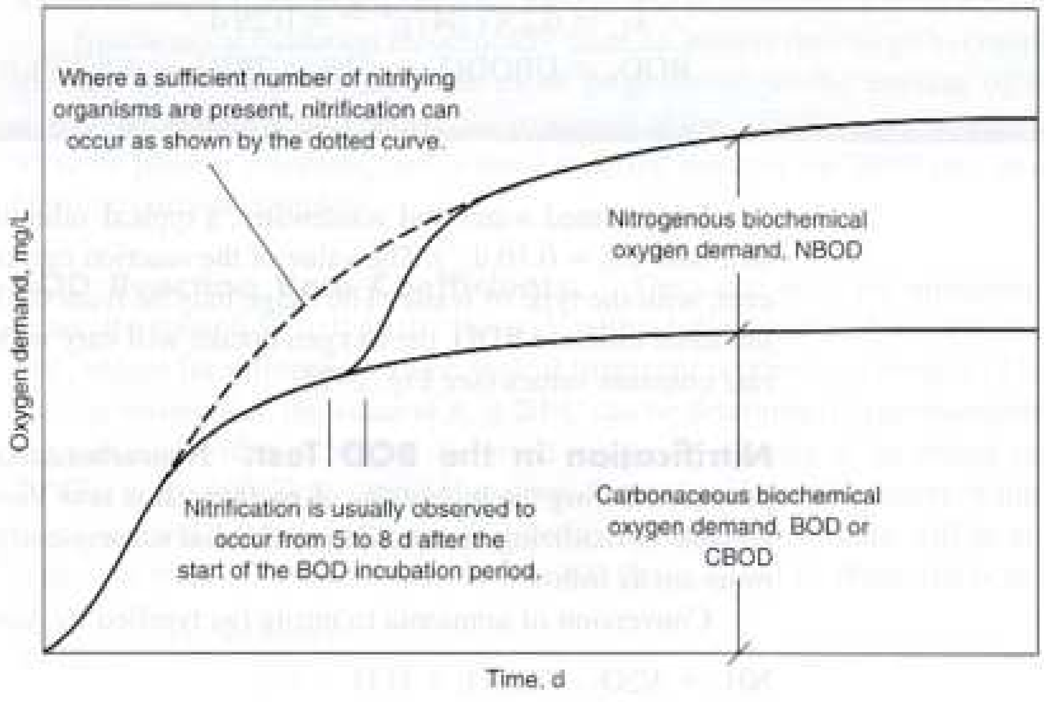
- Ammonia-nitrogen in wastewater may significantly contribute to the total oxygen demand by nitrification:

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$$

#3

Figure 2-24

Definition sketch for the exertion of the carbonaceous and nitrogenous biochemical oxygen demand in a waste sample.



NBOD vs. CBOD

- The oxygen demand associated with the oxidation of ammonia is referred to as nitrogenous biochemical oxygen demand (NBOD)
- Carbonaceous biochemical oxygen demand (CBOD): the oxygen demand associated with the oxidizable carbon in the sample
- When NBOD is significant, nitrification is suppressed by adding chemical agents for the measurement of CBOD

COD

- Measured by oxidizing the organic compounds in water using a strong oxidizing agent
- Oxidizing agent: potassium dichromate ($K_2Cr_2O_7$ - more common) or potassium permanganate ($KMnO_4$)
- Can be fractionated into particulate and soluble COD
  - Soluble COD: readily biodegradable / nonbiodegradable
  - Particulate COD: slowly biodegradable / nonbiodegradable

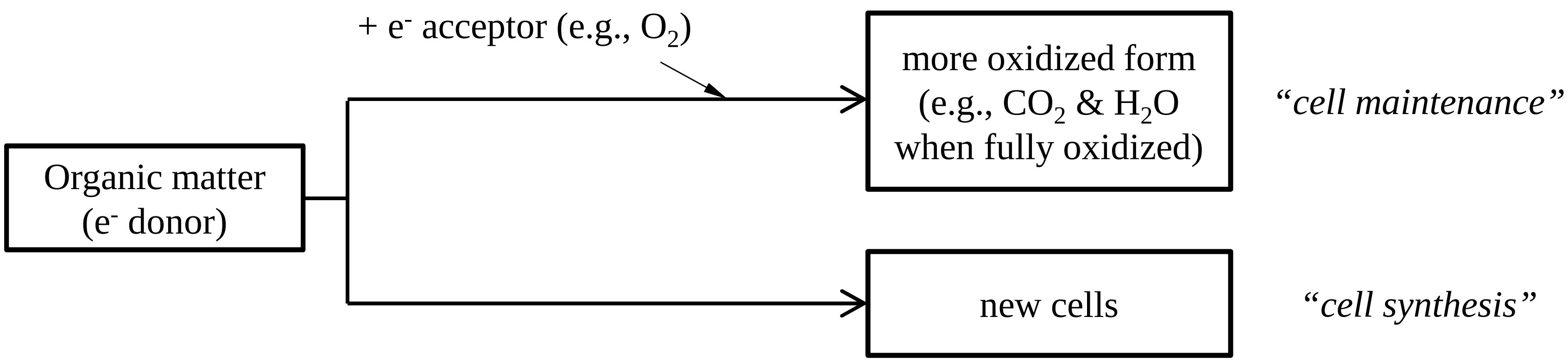
#4

#5

#6

COD vs BOD

- **COD > BOD** because:
  - Many organics that are difficult to be oxidized biologically can be oxidized chemically (ex: lignin)
  - Inorganic substances in water may be oxidized by chemical oxidizing agents
  - Certain organic substances may be toxic to microorganisms used in the BOD test
  - When microorganisms grow, they utilize some fraction of organic compounds to synthesize cells instead of oxidizing them



TOC

TOC Analyzer at Waste Management & Resource Recirculation Lab., SNU

- Measures all organic carbon in a water sample including those that cannot be chemically/biologically oxidized
- Can be fractionated into particulate/soluble TOC
- Three steps for measurement
  - **Acidification**: add acid to reduce the pH → removes carbonate species (inorganic carbon) from water
  - **Oxidation**: use heat, oxygen, ultraviolet radiation, or combination of those to oxidize organic carbon to CO_2
  - **Quantification**: measure the amount of CO_2 production with an infrared analyzer or other means
- TOC: measures amount of **C** / BOD & COD: measures amount of **O_2** consumed by oxidation

  → different COD/TOC ratio for different compounds!

BOD, COD, & TOC

Q: Determine the theoretical ratios of BOD_5/COD and COD/TOC for an organic compound represented by $C_5H_7O_2N$. Use the following assumptions:

- The compound can be completely mineralized biologically
- Only CBOD is considered for BOD
- The BOD first-order reaction rate constant, k_1, is 0.23/d

BOD, COD, & TOC

1) BOD_5/COD

Assume UBOD=COD as the compound can be completely mineralized biologically

$$\frac{BOD_5}{COD} = \frac{BOD_5}{UBOD} = 1 - \exp(-k_1 t) = 1 - \exp(-0.23/d \times 5d)$$

$$\frac{BOD_5}{COD} = 0.68$$

2) COD/TOC

The reaction to completely mineralize the organic compound can be written as

$$C_5H_7O_2N + 5O_2 \rightarrow 5CO_2 + NH_3 + 2H_2O$$

Molecular weight: 113

BOD, COD, & TOC

COD per g compound is calculated as:

$$\frac{5 \times 32\ g\ O_2}{113\ g\ C_5H_7O_2N} = 1.42\ g\ COD/g\ C_5H_7O_2N$$

This value will be utilized later in this class for modeling biological wastewater treatment!

TOC per g compound is calculated as:

$$\frac{5 \times 12\ g\ C}{113\ g\ C_5H_7O_2N} = 0.53\ g\ TOC/g\ C_5H_7O_2N$$

$$\frac{COD}{TOC} = \frac{1.42}{0.53} = 2.68$$

BOD, COD, & TOC

cf) CH_4 (methane) COD/TOC value

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

COD per g CH_4:

$$\frac{2 \times 32\ g\ O_2}{16\ g\ CH_4} = 4.0\ g\ COD/g\ CH_4$$

TOC per g CH_4:

$$\frac{1 \times 12\ g\ C}{16\ g\ CH_4} = 0.75\ g\ TOC/g\ CH_4$$

$$\frac{COD}{TOC} = \frac{4.0}{0.75} = 5.33$$

COD/TOC ratio is much higher for CH_4 than for $C_5H_7O_2N$ (2.68). Can you find the reason why?

Individual organic compounds

- Some organic compounds have particular toxicity to humans and aquatic organisms → have to be regulated individually
- Sources
  - Commercial and industrial wastewater
  - Disinfection byproducts
  - Surface runoff from agricultural land (ex: pesticides)
  - Surface runoff from urban area (ex: oil spill, additives used for vehicles, sealant for pavements)
  - Pharmaceuticals and personal care products (PPCPs)
    - Mostly not regulated currently, but of recent interest

#7

#8

References

#1) https://www.youtube.com/watch?v=yq7lSeCi6uo

#2) https://www.ysi.com/ysi-blog/water-blogged-blog/2013/02/bod-testing-accuracy-and-success-are-you-achieving-this

#3) Metcalf & Eddy, Aecom (2014) Wastewater Engineering: Treatment and Resource Recovery, 5^{th} ed. McGraw-Hill, p. 120.

#4) https://www.fishersci.fi/shop/products/sulfate-test-kits/11781093

#5) http://www.wealtec.com/products/basic/block-heater/hb-2.htm

#6) https://www.wateronline.com/doc/cod-reagent-vials-0002

#7) https://www.istc.illinois.edu/research/pollutants/PPCPs_in_the_environment

#8) https://www.webpackaging.com/en/portals/serioplast/assets/11219484/personal-care-pharmaceuticals/