Chemical characteristics of water II

Today's class

- Gross indicators of organic content
  - Biochemical oxygen demand (BOD)
  - Chemical oxygen demand (COD)
  - Total organic carbon (TOC)

- Individual organic compounds

Organic compounds in water

- 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

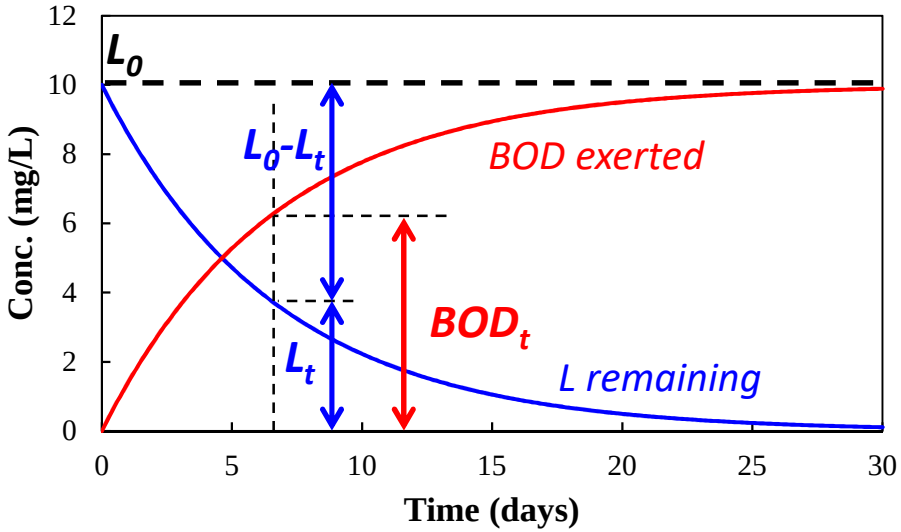
- **BOD test procedure**
  - The water sample is diluted such that the difference between the DO before and after the test can be determined (estimated BOD: 2-6 mg/L)
  - The diluted water sample is inoculated with microorganisms that degrade organic matter
  - The diluted, inoculated water sample is 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

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)

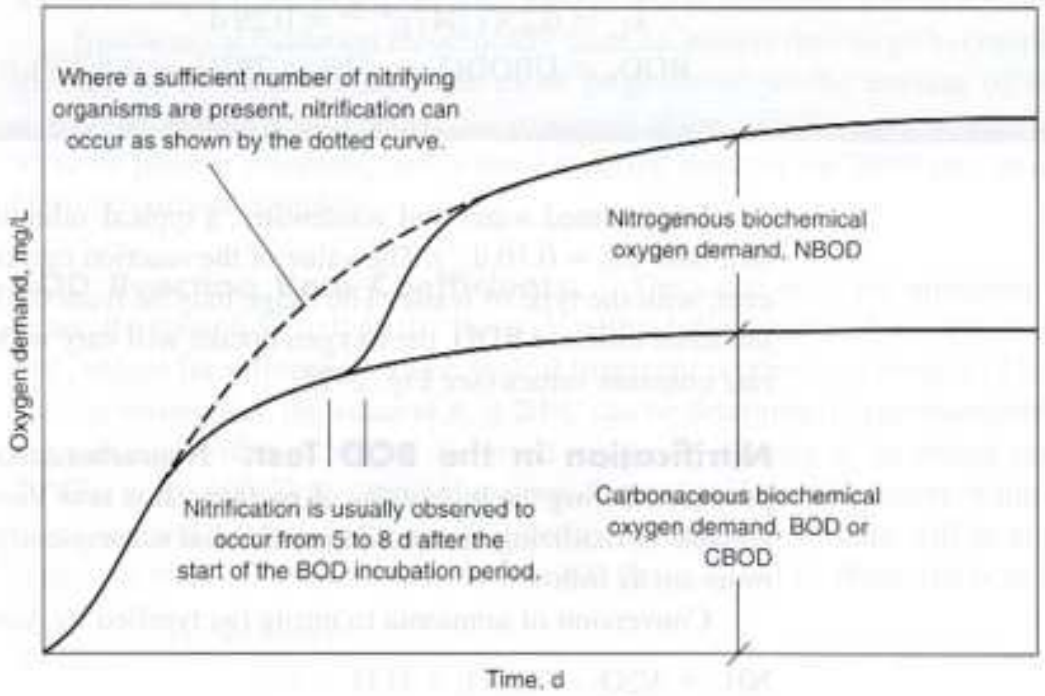
NBOD vs. CBOD

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

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

Figure 2-24

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



NBOD vs. CBOD

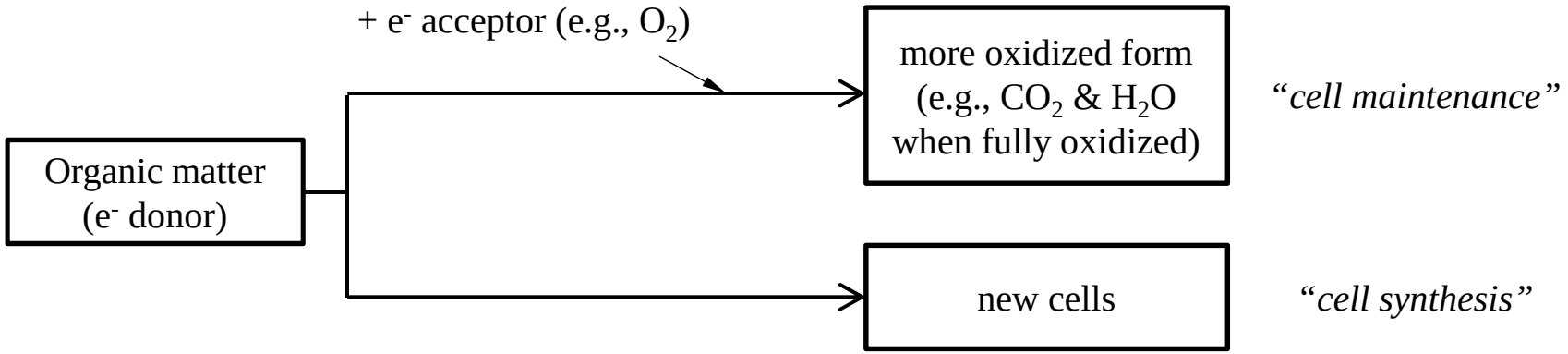
- The oxygen demand associated with the oxidation of ammonia is referred to as nitrogenous biochemical oxygen demand (NBOD)
- Carbonaceous biochemical oxygen demand (CBOD): the oxygen demand associated with the oxidizable carbon in the sample
- When NBOD is significant, nitrification is suppressed by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

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

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

Formula 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




Korean regulatory standards: COD → TOC

하수도법 시행규칙

[공공하수처리시설의 방류수 수질기준] (2022. 12. 9. 개정)

1. 방류수 수질기준

1) 2011년 1월 1일부터 2019년 12월 31일까지 적용되는 기준

구 분	적용기간 및 수질기준								
	2011. 1. 1. 부터 2011. 12. 31. 까지	2012. 1. 1.부터 2012. 12 .31. 까지				2013. 1. 1.부터 2019. 12. 31. 까지			
		Ⅰ지역	Ⅱ지역	Ⅲ지역	Ⅳ지역	Ⅰ지역	Ⅱ지역	Ⅲ지역	Ⅳ지역
생물화학적 산소요구량 (BOD) (mg/L)	20(30) 이하	20(30) 이하	20(30) 이하	20(30) 이하	20(30) 이하	10(10) 이하	10(10) 이하	10(10) 이하	10(10) 이하
화학적 산소요구량 (COD) (mg/L)	40(40) 이하	40(40) 이하	40(40) 이하	40(40) 이하	40(40) 이하	20(40) 이하	20(40) 이하	40(40) 이하	40(40) 이하
부유물질 (SS) (mg/L)	20(30) 이하	20(30) 이하	20(30) 이하	20(30) 이하	20(30) 이하	10(10) 이하	10(10) 이하	10(10) 이하	10(10) 이하
총질소 (T-N) (mg/L)	40(60) 이하	40(60) 이하	40(60) 이하	40(60) 이하	40(60) 이하	20(20) 이하	20(20) 이하	20(20) 이하	20(20) 이하
총인									

2) 2020년 1월 1일부터 적용되는 기준

구 분	수질기준			
	Ⅰ지역	Ⅱ지역	Ⅲ지역	Ⅳ지역
생물화학적 산소요구량 (BOD) (mg/L)	10(10) 이하	10(10) 이하	10(10) 이하	10(10) 이하
총유기 탄소량 (TOC) (mg/L)	15(25) 이하	15(25) 이하	25(25) 이하	25(25) 이하
부유물질 (SS) (mg/L)	10(10) 이하	10(10) 이하	10(10) 이하	10(10) 이하
총질소	20(20)	20(20)	20(20)	20(20)

Key references

- Textbook sec 2-6, 2-7

Next class

- Biological characteristics of water
  - Types of microorganisms
  - Cell components, genetic molecules, enzymes
  - Classification of organisms
  - Analyzing genetic molecules of organisms
  - Enumeration and identification of bacteria