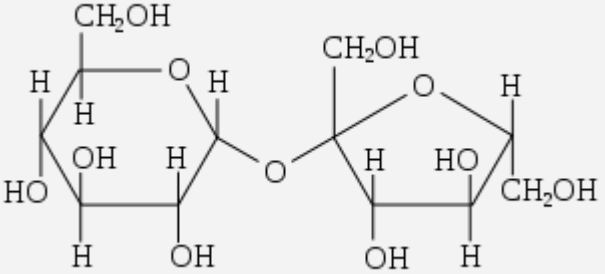
# Quantifying organics: COD & BOD

*CTB3365x Introduction to water treatment*

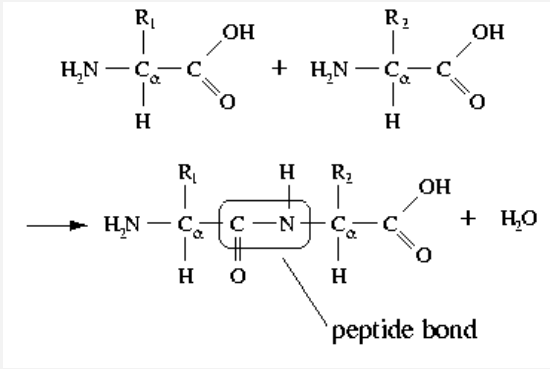
Prof.dr.ir. Jules B. van Lier

# Organic matter in sewage

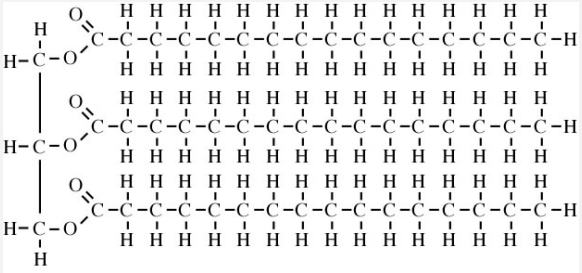
1. Sugars




2. Proteins




3. Fats



# Chemical Oxygen Demand (COD)

***Measurement:***

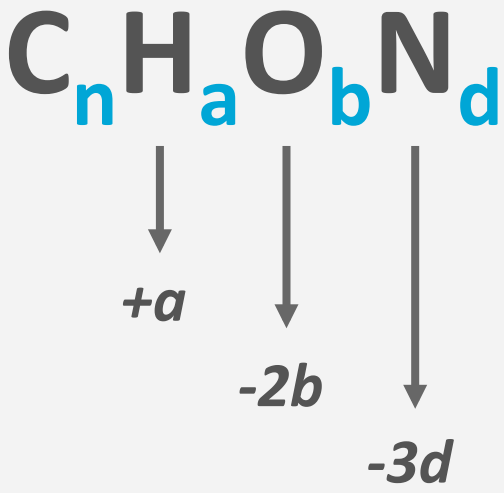
- Bi-chromate ($K_2Cr_2O_7$) as oxidizing agent
- High temp.: 150°C
- Sulphuric acid

COD lab test set-up

# Chemical Oxygen Demand (COD)

***The 'theoretical COD' calculation of organic compound***

- Based on a complete oxidation
- Required amount of $O_2$ depends on oxidation state of C




***Oxidation state:***

$$\frac{2b + 3d - a}{n}$$

# Chemical Oxygen Demand (COD)

***The number of electrons made free per C atom in complete oxidation of $C_nH_aO_bN_d$:***

$4-(\frac{2b+3d-a}{n})$ , As +4 is the most oxidized form of C ($CO_2$)

# Chemical Oxygen Demand (COD)

***Complete oxidation of organic matter to $CO_2$ and $H_2O$:***

- $C_nH_aO_bN_d$ → ***Note: both O and N (!) stay reduced. In the COD test N is converted to $NH_3$***

***The required amount of $O_2$ molecules for the complete oxidation:***

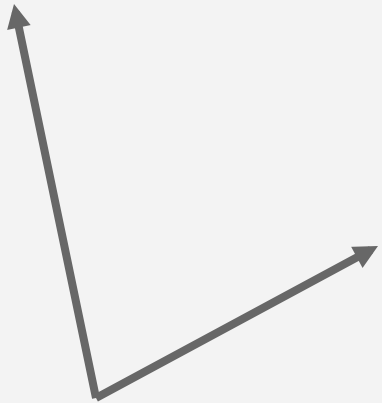
- $C_nH_aO_bN_d + ¼\ (4n+a-2b-3d)\ O_2 \rightarrow n\ CO_2 + ½(a-3d)\ H_2O + d\ NH_3$

  *1 $O_2$ accepts max. 4 electrons*

# Chemical Oxygen Demand (COD)

***1 mole of organic matter demands:***

- *¼ (4n+a-2b-3d)* moles **$O_2$** or *8(4n+a-2b-3d)* grams **$O_2$**



***Theoretical COD calculation:***

$$COD_t = \frac{8(4n + a - 2b - 3d)}{12n + a + 16b + 14d} \quad \frac{\text{mg COD}}{\text{mg } C_nH_aO_bN_d}$$

- $C_nH_aO_bN_d + ¼\ (4n+a-2b-3d)\ O_2 \rightarrow n\ CO_2 + ½(a-3d)\ H_2O + d\ NH_3$

# Total Organic Compound (TOC)

***TOC: Organic matter measured as $CO_2$ after incineration***

- (Corrections needed for inorganic carbon in waste sample)
- $$\mathrm{TOC_t} = \frac{12n}{12n + a + 16b + 14d} \quad \frac{\mathrm{g\ TOC}}{\mathrm{g\ C_nH_aO_bN_d}}$$

# g COD and g TOC per g organic compound (no N)

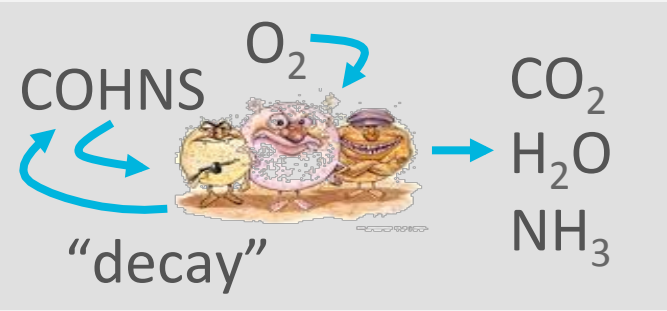
***Ratio COD/TOD:*** $\frac{8(4n+a-2b-3d)}{12n} = \frac{8}{3} + \frac{2(a-2b-3d)}{3n}$

| Compound | n | a | b | g COD ($g\ C_nH_aO_b$) | g TOC ($g\ C_nH_aO_b$) | COD/TOC ratio |
|---|---|---|---|---|---|---|
| Oxalic acid | 2 | 2 | 4 | 0.18 | 0.27 | 0.67 |
| Formic acid | 1 | 2 | 2 | 0.35 | 0.26 | 1.33 |
| Citric acid | 6 | 8 | 7 | 0.75 | 0.38 | 2.00 |
| Glucose | 6 | 12 | 6 | 1.07 | 0.40 | 2.67 |
| Lactic acid | 3 | 6 | 3 | 1.07 | 0.40 | 2.67 |
| Acetic acid | 2 | 4 | 2 | 1.07 | 0.40 | 2.67 |
| Glycerine | 3 | 8 | 3 | 1.22 | 0.39 | 3.11 |
| Phenol | 6 | 6 | 1 | 2.38 | 0.77 | 3.11 |
| Ethylene glycol | 2 | 6 | 2 | 1.29 | 0.39 | 3.33 |
| Benzene | 6 | 6 | 0 | 3.08 | 0.92 | 3.33 |
| Acetone | 3 | 6 | 1 | 2.21 | 0.62 | 3.56 |
| Palmitic acid | 16 | 32 | 2 | 3.43 | 0.75 | 3.83 |
| Cyclohexane | 6 | 12 | 0 | 3.43 | 0.86 | 4.00 |
| Ethylene | 2 | 4 | 0 | 3.43 | 0.86 | 4.00 |
| Ethanol | 2 | 6 | 1 | 2.09 | 0.52 | 4.00 |
| Methanol | 1 | 4 | 1 | 1.50 | 0.38 | 4.00 |
| Ethane | 2 | 6 | 0 | 3.73 | 0.80 | 4.67 |
| Methane | 1 | 4 | 0 | 4.00 | 0.75 | 5.33 |

# Biochemical Oxygen Demand (BOD)

***Oxidation***

- COHNS + **$O_2$** → $CO_2$ + $H_2O$ + NH + *energy*




***Synthesis***

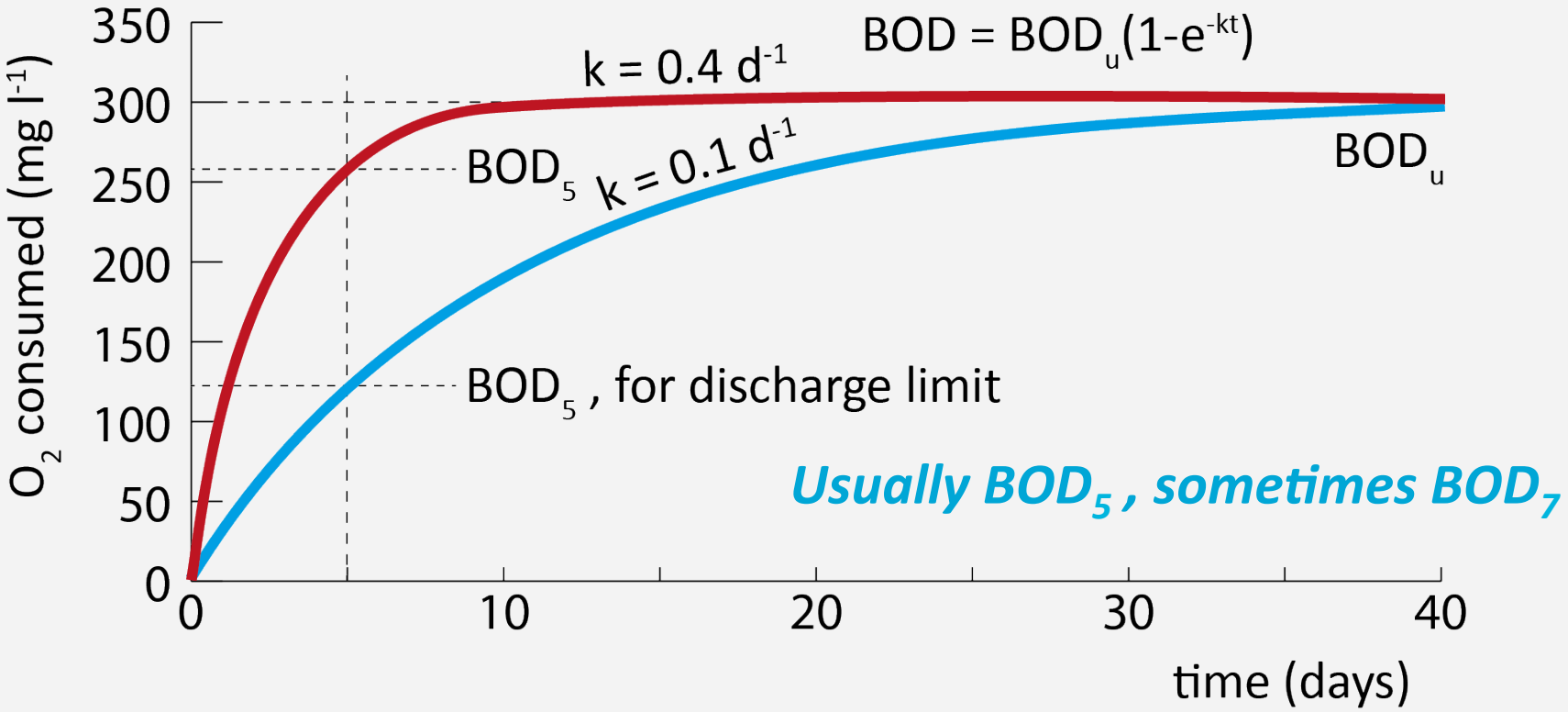
- COHNS + **$O_2$** + *bacteria* + *energy* → **$C_5H_7NO_2$**

***"Endogenous respiration (decay)"***

- **$C_5H_7NO_2$** + 5 **$O_2$** → 5 $CO_2$ + $NH_3$ + 2 $H_2O$ : **mineralization products**

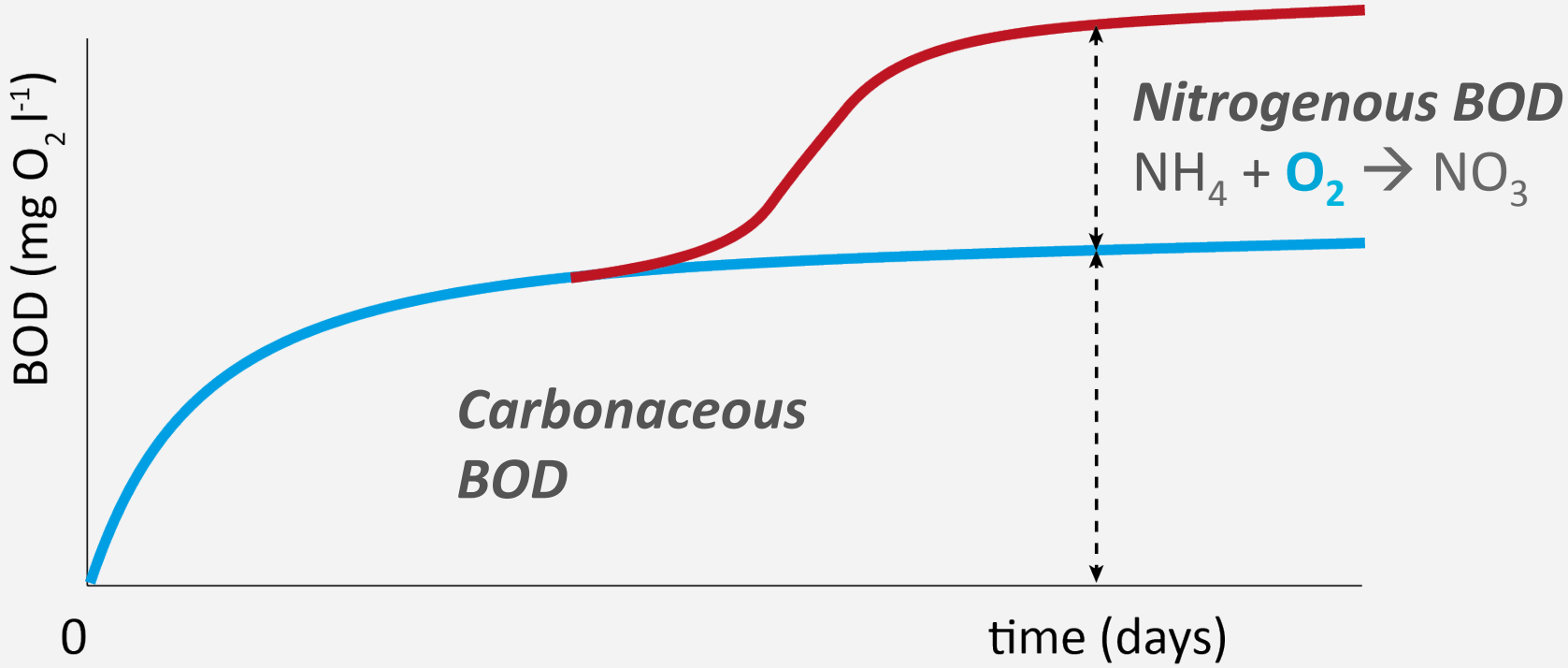
***Ultimate $BOD_u$ = sum of all $O_2$ to mineralize organic matter***

# Biochemical Oxygen Demand (BOD)

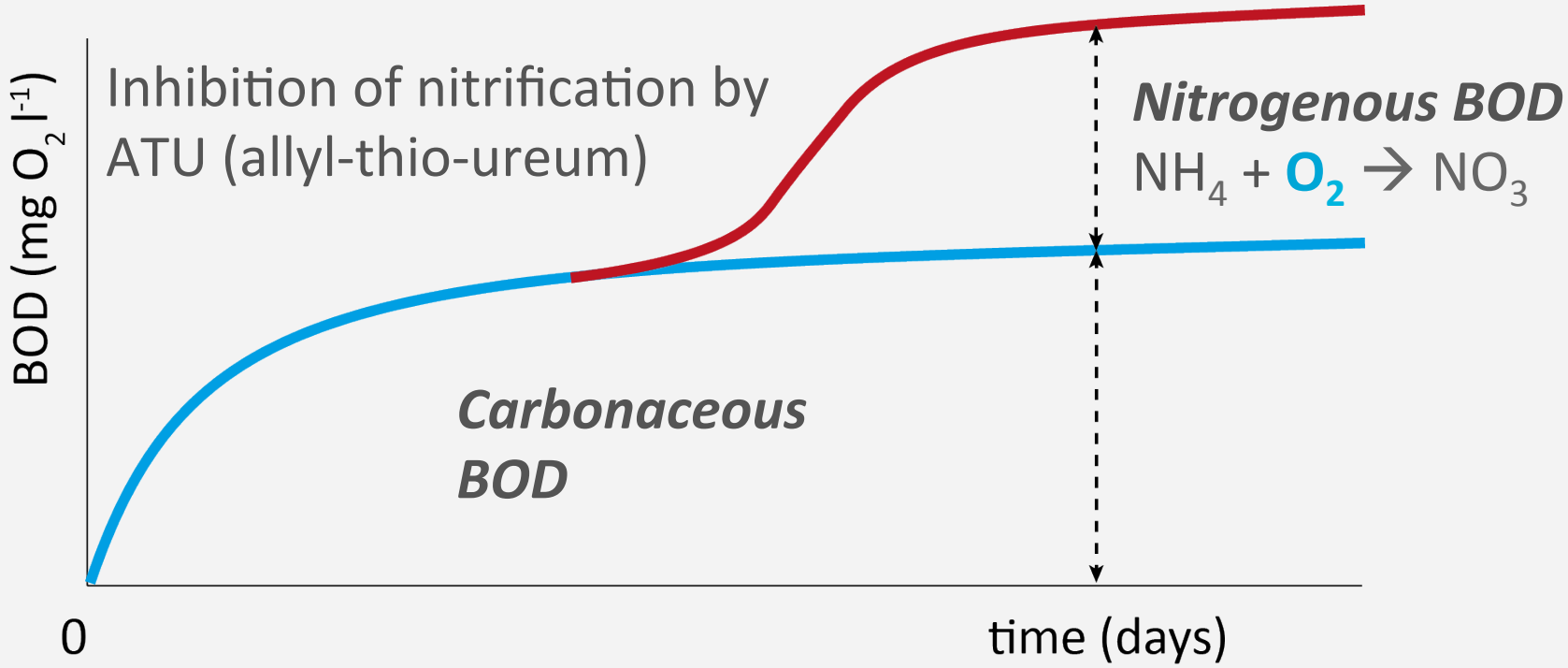



***Usually $BOD_5$ , sometimes $BOD_7$***

# Biochemical Oxygen Demand (BOD)



# Biochemical Oxygen Demand (BOD)



# Biochemical Oxygen Demand (BOD)

- Determines size of wastewater treatment plant
- Resembles $O_2$ requirement to stabilize organic matter
- Compliance with discharge permits
- Measure efficiency treatment plant

***EU sewage:*** ***- 110 – 350 mg BOD $l^{-1}$***

***- BOD/COD ratio ≈ 0.5***

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