Environment Chemistry

pH

A Conventional Perspective

Lecture 10

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Presentation Menu

- Introduction
- Nature of BOD reaction
- Methodology
- Rate of biochemical oxidations
- Examples on calculations

Introduction

BOD amount of oxygen required by bacteria while stabilizing decomposable organic matter under aerobic conditions.

Decomposable organic matter that can serve as food for bacteria, and energy is derived from its oxidation

BOD measure pollution strength of wastewater or polluted water

Introduction

BOD the most important in stream-pollution-control activities

BOD important in regulatory work

BOD test bioassay procedure involving the measurement of oxygen consumed by living organisms (mainly bacteria) while utilizing organic matter present in a waste, under conditions as similar as possible to nature.

Concept for BOD test

- Wet oxidation procedure in which living organisms serve as the medium for oxidation of the organic matter to CO_2 and water.
- Generalized equation:

$$C_nH_aO_bN_c + \left(n + \frac{a}{4} - \frac{b}{2} - \frac{3}{4}c\right)O_2 \rightarrow nCO_2 + \left(\frac{a}{2} - \frac{3}{2}c\right)H_2O + cNH_3$$

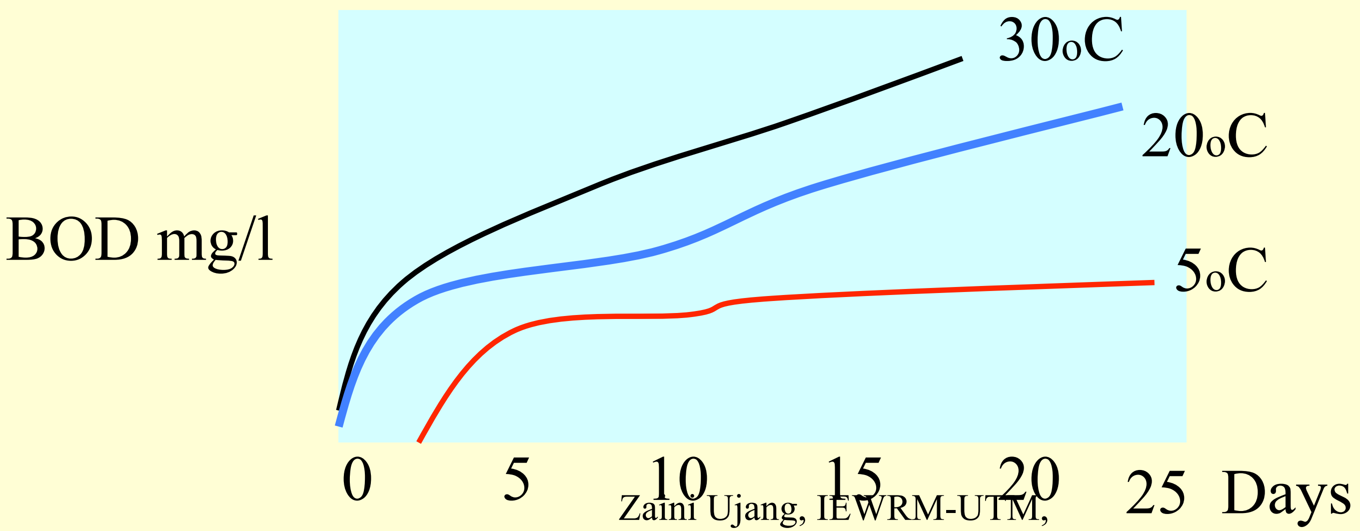
Organic matters

Time for BOD test

- Theoretically an infinite time is required for complete biological oxidation of organic matter, but for practical purposes, the reaction may be considered complete in 20 days.
- But for practical reasons, 5 days was used since large percentage of the total BOD is exerted in 5 days.
- 5 days BOD values only represent a portion of the total BOD values.
- For most industrial and municipal wastewater, the 5-day BOD value is about 70 to 80 percent of the total BOD.

Temperature for BOD test

- Temperature effects for microbial dynamics are constant at 20$_o$C.
- Predominant organisms responsible for the stabilization of organic matter in natural waters are forms native to the soil.



Nature of the BOD Reaction …

First order kinetics

The rate of the reaction is proportional to the amount of oxidizable organic matter remaining at any time, as modified by the population of active organisms

Once the population of organisms has reached a level at which only minor variations occur, the reaction rate is controlled by the amount of food available to the organisms:

$$-\frac{dC}{dt} \alpha\ C$$

$$-\frac{dC}{dt} = k'C$$

C = concentration of oxidizable organics (pollutants) at the start of the time interval, t

k'= rate constant for the reaction

…Nature of the BOD Reaction

L is normally to replace C in BOD terms
L represents the ultimate demand:

$$-\frac{dL_t}{dt} = kL_t$$

-dL/dt = the rate at which organic polluting matter is destroyed

Oxygen is used in stabilizing organic matter in direct ratio to the amount of organics oxidized, it is possible to interpret L in terms of organic matter , or in terms of oxygen used.

...Nature of the BOD Reaction

$$\frac{dL_t}{dt} = -kL_t$$

$$\frac{dL_t}{L_t} = -kdt$$

$$\int_{L_o}^{L} \frac{dL_t}{L_t} = -k \int_{o}^{t} dt$$

$$\ln \frac{L_t}{L_o} = -kt$$

$$L_t = L_o e^{-kt}$$

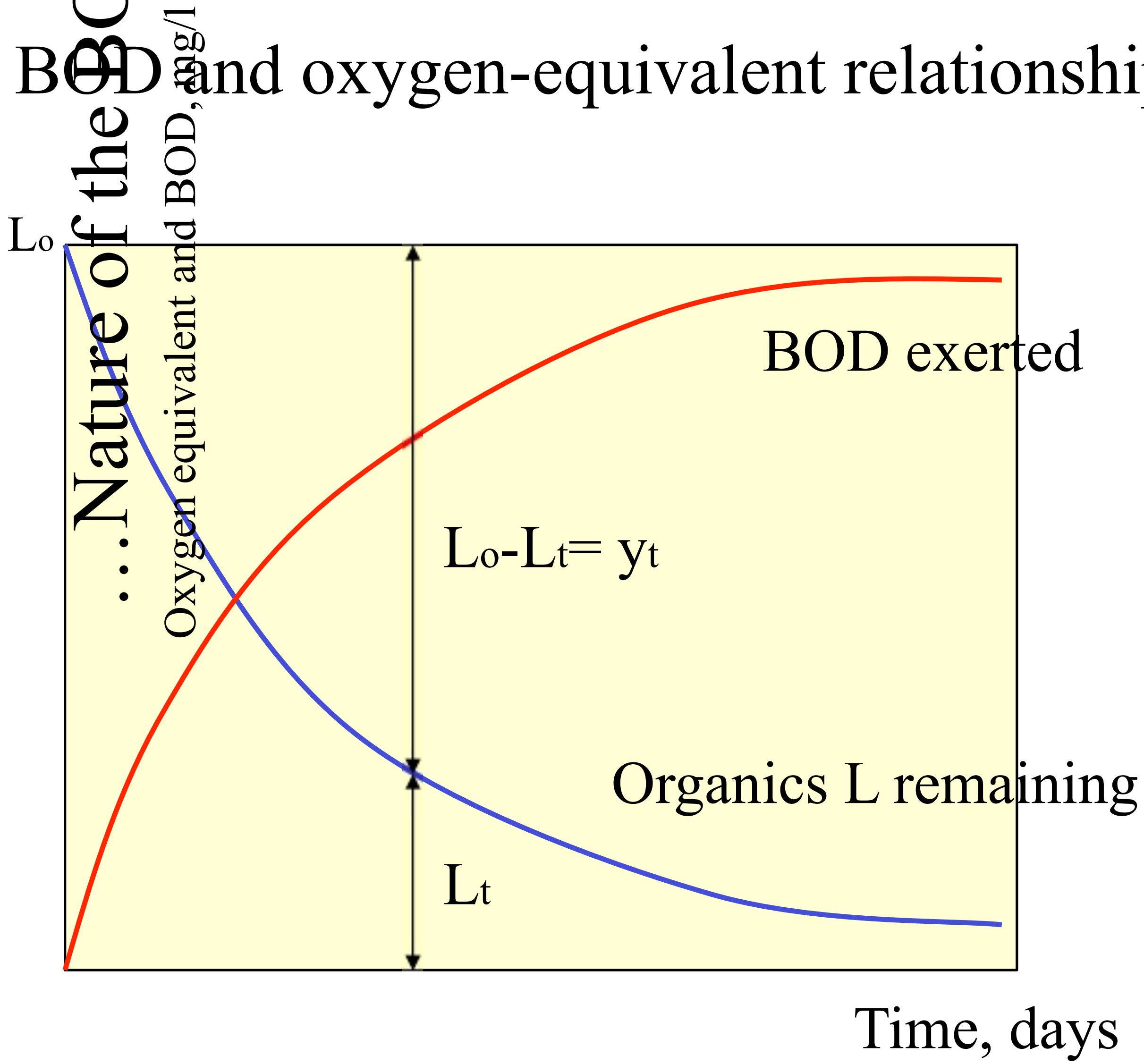
L_t = oxygen equivalent of the organics at time t

k = reaction constant, d^{-1}

L_o = total oxygen equivalent of organics at time 0

…Nature of the BOD

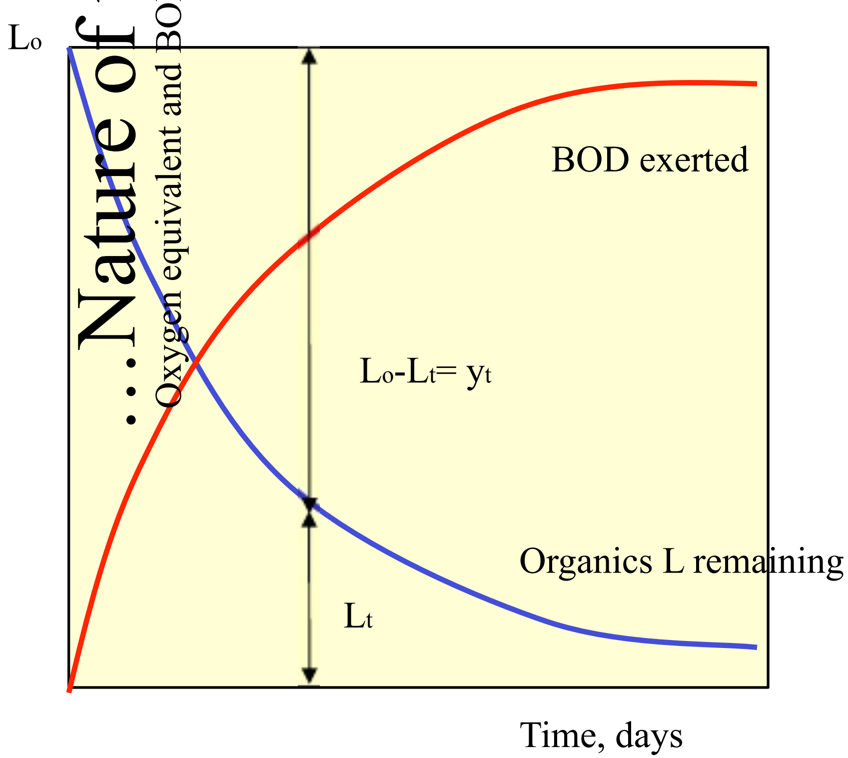
BOD and oxygen-equivalent relationships



$$\frac{-dC}{dt} = k'C$$

…Nature of the BOD

BOD and oxygen-equivalent relationships



$$y_t = L_o - L_t$$

$$y_t = L_o - L_o e^{-kt}$$

$$y_t = L_o\left(1 - e^{-kt}\right)$$

Y_t = BOD_t of the water samples

…Nature of the BOD Reaction

Environmental engineers are more interested on BOD exerted.

Test – using dissolved-oxygen measurements

Use 5-day result to total or ultimate BOD (y_u) or BOD at some other time:

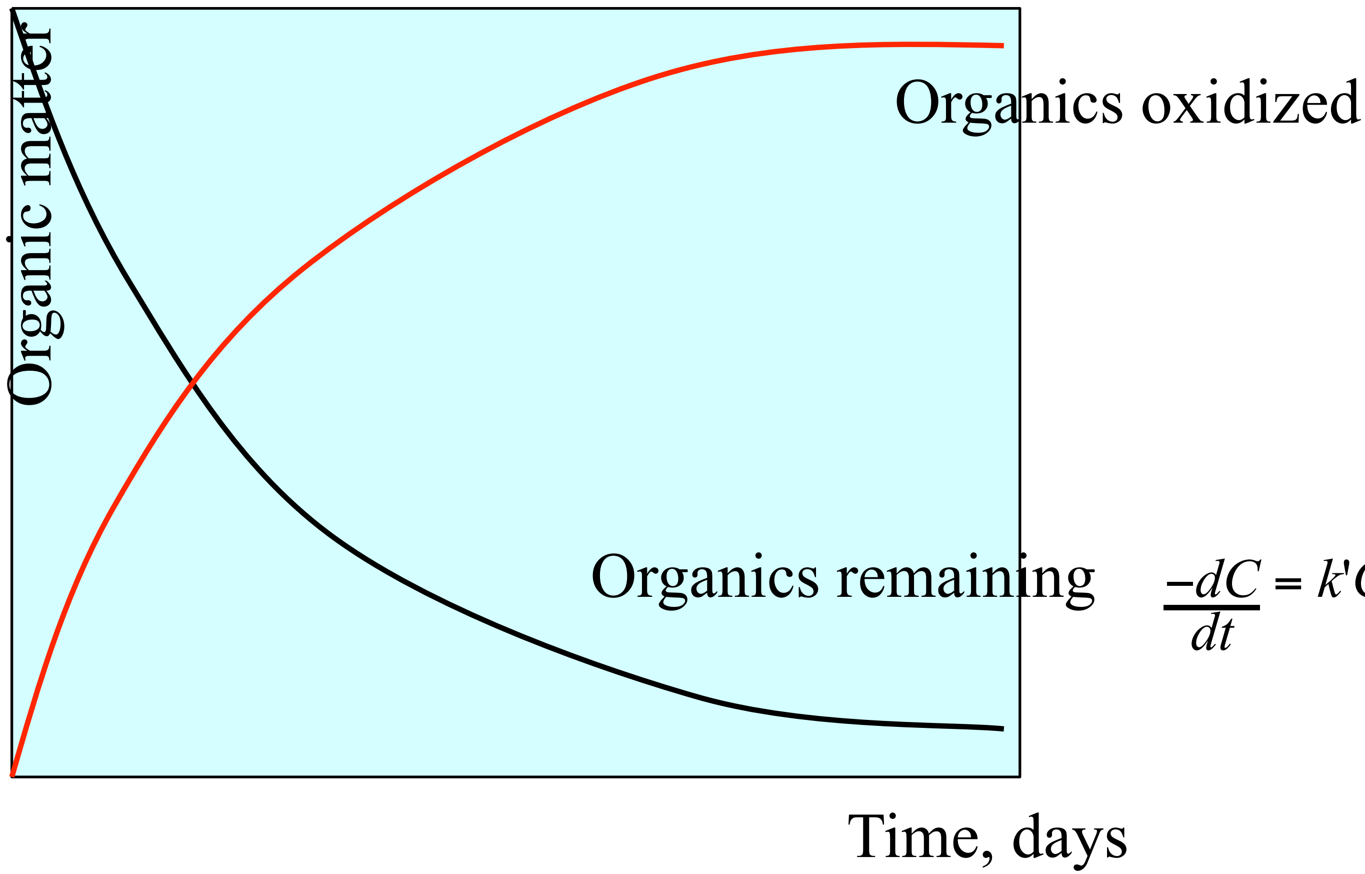
$$y_t = L_o\left(1 - e^{-kt}\right)$$

y = BOD at any time t

L = total or ultimate BOD

k = determine by experiment

Changes in organics during biological oxidization of polluted waters under aerobic conditions

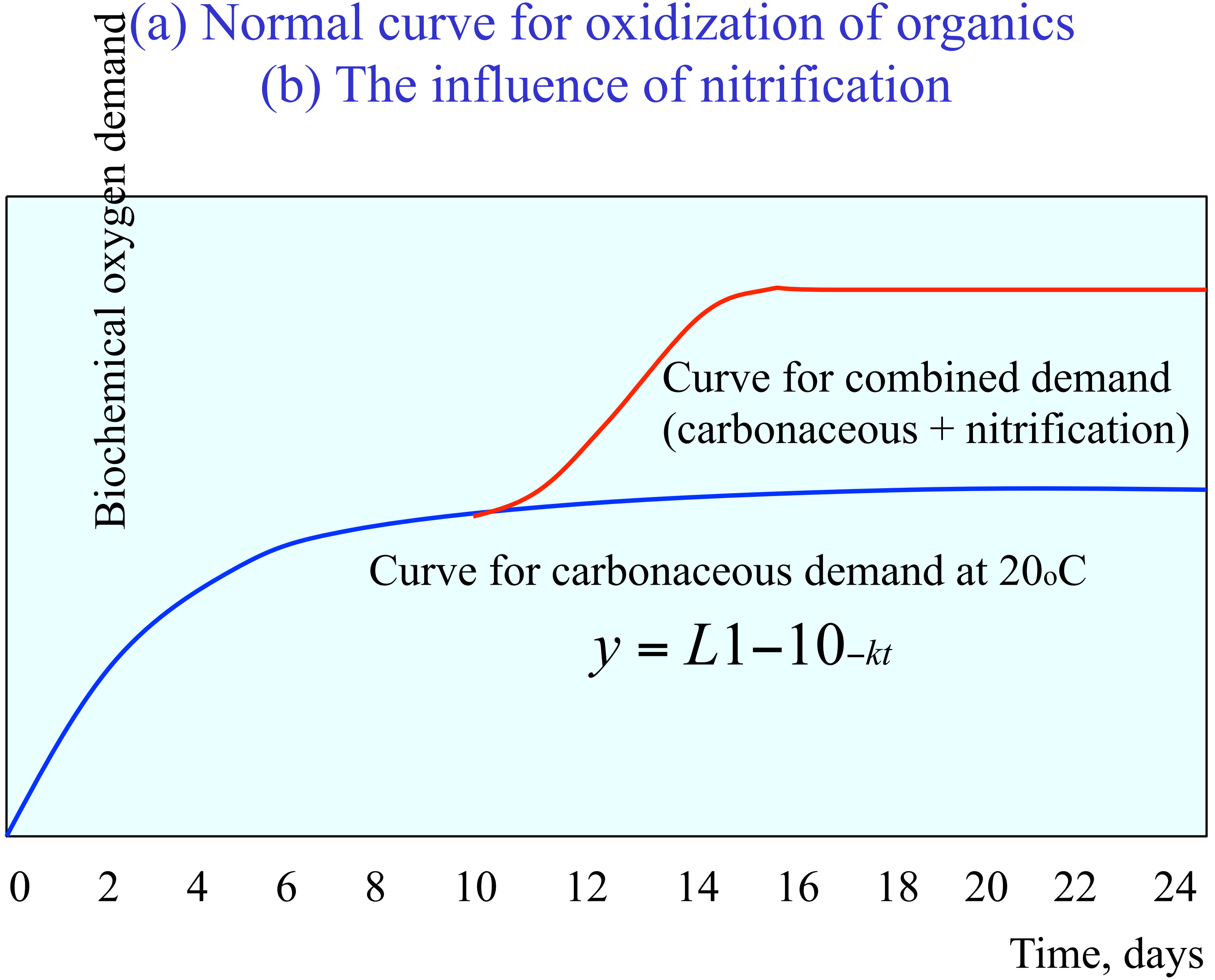


$$\frac{-dC}{dt} = k'C$$

The BOD curve:

(a) Normal curve for oxidization of organics

(b) The influence of nitrification



Reaction constant

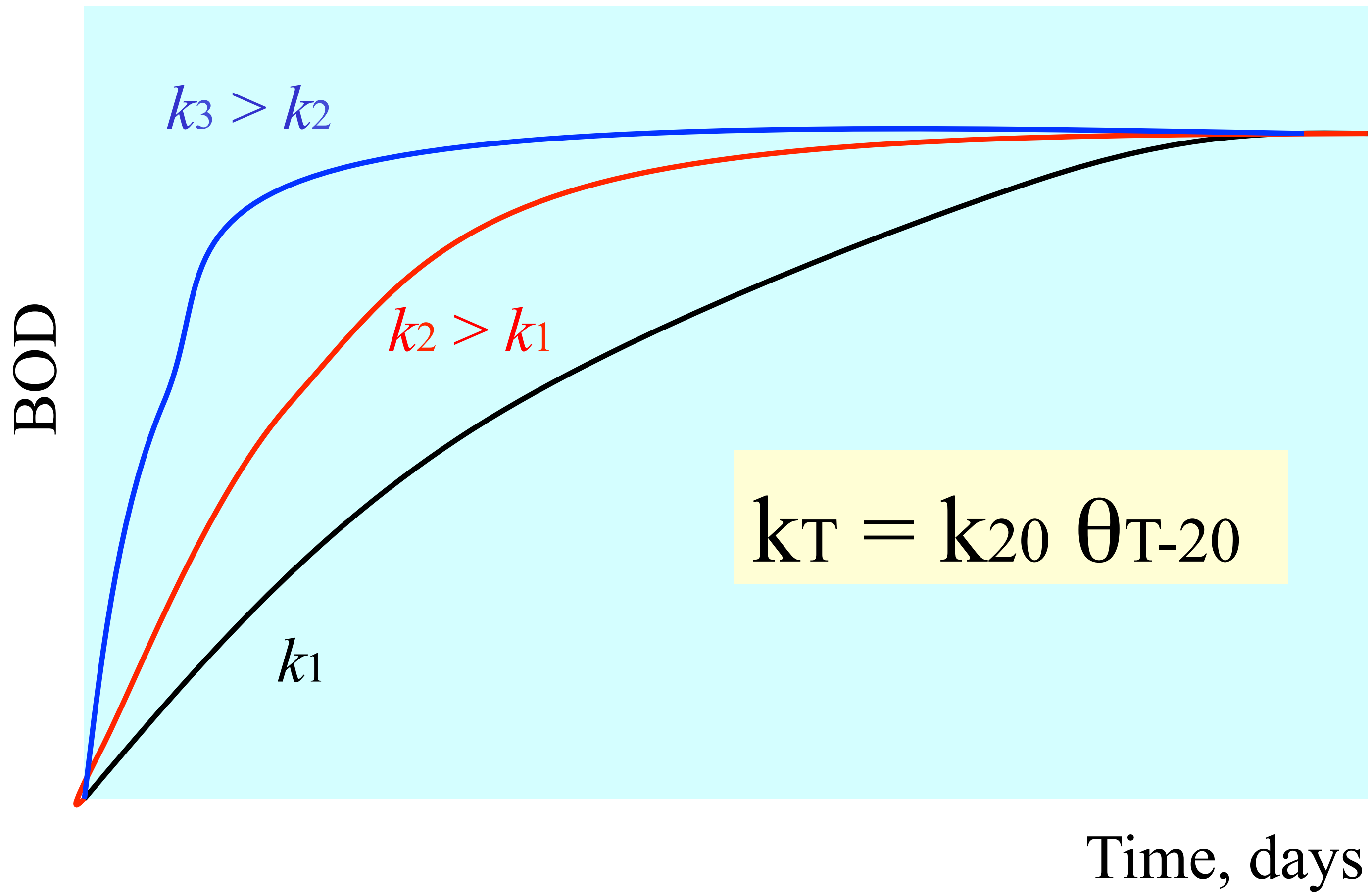
- Value of *k* (in some books, ∝) determines the speed of the BOD reaction without influencing the magnitude of the ultimate BOD.
- k = 0.1 to 0.5 per day depending on the nature of the organic molecules.
- Simple sugars have high values of *k* rate, vice versa.

Reaction constant

Water type	k, per day (base e)	y_u, mg/l
Tap water	<0.1	0-1
Surface water	0.1-0.23	1-30
Weak municipal wastewater	0.35	150
Strong municipal wastewater	0.40	250
Treated effluent	0.12-0.23	10-30

Reaction constant

k is temperature-dependent, because microorganisms are more active at high temperature, where *k* values are higher.



Nitrification-Denitrification

Nitrogenous BOD

Nitrite-forming

bacteria

2

Nitrate-forming

$$2NO_2^- + O_2 + 2H^+ \xrightarrow[\text{bacteria}]{} 2NO_3^- + 2H^+$$

Nitrification-Denitrification

Nitrogenous BOD

- The interference cause by nitrifying bacteria makes the actual measurement of total carbonaceous BOD impossible unless provision is made to eliminate them.
- Nitrifying bacteria was the major reason for selecting 5-day for BOD test.
- For samples with high concentration of nitrifying bacteria use the following inhibiting agent:

2-chloro-6-(tricholoro methyl)pyridine (TCMP)

Method for Measuring BOD

Basis: determinations of dissolved oxygen
Methods:

a) Direct method for 5-day BOD < 7 mg/l
b) Dilution method for samples >> 7 mg/l

BOD test again!

Dilution method

- Polluted water is mixed with clean aerated water
- The mixture is poured into a bottle which is sealed so that there is no air above the liquid.
- The microorganisms in the polluted water consume oxygen, and it is necessary to ensure that oxygen is present for the process within the 5-day.
- If the oxygen is depleted, or if its concentration bacomes low, the measuring result cannot be used.
- Therefore requires more dilution!!

BOD test again!

Calculated values

- Based on 5-day oxygen demand and the volume of polluted water in the laboratory flask, the BOD can be calculated:

$$BOD = \frac{DO_I - DO_F}{P}$$

DO_I, DO_F = initial and final dissolved oxygen, mg/l
P = decimal fraction of sample in the 300-ml bottle

Example: Calculation of BOD values

- The BOD of a wastewater is suspected to range from 50 to 200 mg/l. Three dilutions are prepared to cover this range. The procedure is the same in each case. First the sample is placed in the standard BOD bottle and is then diluted to 300 ml with organic-free, oxygen-saturated water. The initial DO is determined and the bottles tightly stoppered and placed in the incubator at 20$_o$C for 5 days, after which the DO is again determined. If the third value is disregarded (the final DO being less than 2 mg/l), calculate the average BOD.

BOD Calculation

Wastewater, ml	DO_I, mg/l	DO_F, mg/l	O_2 used, mg/l	P	BOD_5, mg/l
5	9.2	6.9	2.3	0.0167	138
10	9.1	4.4	4.7	0.033	142
20	8.9	1.5	7.4	0.067	110

If the third value is disregarded (final DO is less than 2 mg/l) then the average BOD value is (138 + 142)/2 = 140 mg/l

Example: BOD conversion

Question: The BOD_5 of a wastewater is determined to be 150 mg/l at 20_oC. The k value is known to be 0.23 per day. What would be the BOD_8 be if the test were run at 15_oC?

a) Determine the ultimate BOD:

$$y_u = \frac{y_5}{1 - e^{-kt}}$$

$$y_u = \frac{150}{1 - e^{-0.23x5}} = 220 mg/l$$

Example: BOD conversion

b) Correct the k value for 15_{o}C:

$$k_T = k_{20}\theta^{T-20}$$

$$k_{15} = 0.23(1.047^{-20}) = 0.18$$

c) Calculate y_8:

$$-kt$$

$$y_8 = 220\left(-e_{0.18x8}\right) = 168 mg/l$$

Process Theory

(ii) Plug-flow reactor