BIOLOGICA L'OODGROVE BANK OXYGEN DEMAND

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CHEMICAL KINETICS OF BOD

Consider that the decomposition of organic waste in waste water by the microorganism is a first order reaction.

Let, after time 't', the concentration of oxygen be L_t

According to first order rate reaction, rate of the reaction is directly proportional to the concentration of reactant (here oxygen) left at that time(t).

$$-\frac{dL_t}{dt} \propto L_t \qquad \dots (1)$$

The negative sign (–) is indicating that along with time (t) the concentration of oxygen decreases.



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We can rearrange the equation (1) as

$$-\frac{dL_t}{dt} = kL_t; \text{ where, } k = BOD \text{ reaction constant}$$

or,
$$-\frac{dL_t}{L_t} = k dt. \qquad \dots (2)$$

Integrate the above equation within the limit.

When,
$$t = 0$$
, $L_t = L_0$

And
$$t = t$$
, $L_t = L_t$

So, equation (2) becomes

$$-\int_{L_0}^{L_t} \frac{dL_t}{L_t} = k \int_0^t dt$$

or,
$$\left[\ln L_t \right]_{L0}^{Lt} = -k \left[t - o \right]$$

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

or,
$$\frac{L_t}{L_o} = e^{-kt}$$

$$L_o$$

$$L_t = L_0 e^{-kt} \qquad \dots (3)$$

Now, ultimate oxygen demand (L_0) is the sum of the amount of oxygen already consumed by the microorganism for the decomposition i.e. Biological Oxygen Demand at that time (BOD_t) and the concentration of oxygen left for the consumption at that time (L_t) .

So,
$$L_0 = BOD_t + Lt$$

or $BOD_t = L_0 - L_t$
 $= L_0 - L_0 e^{-kt}$ [Put the value of L_t from equation (3)]
or $BOD_t = L_0 \left(1 - e^{-kt}\right)$

THE BOD REACTION RATE CONSTANT (K)

- The BOD reaction rate constant (k) is a factor that indicates the rate of decomposition of wastes. As k increases, the rate at which dissolved oxygen is consumed increases, although the ultimate amount required for the decomposition i.e. ultimate oxygen demand (L₀), does not change. The reaction rate (k) will depend on a number of factors, these are:
- i) the nature of the waste itself
- ii) the ability of the available microorganisms to degrade the waste
- iii) the temperature.

The rate of decomposition of wastes increases with increasing temperature. To account for these changes, the reaction rate constant k is often modified using the following equation –

$$K_T = K_{20}\theta^{(T-20)} - (1)$$

where, $K_{20} \Rightarrow$ reaction rate constant at 20 $^{\circ}$ C

 $K_T \Rightarrow$ reaction rate constant at any temp. (°C)

 $\theta \Rightarrow$ (constant) 1.047.

DE-OXYGENATION

The decomposition of organic waste in waste water by the microorganism is a first order reaction.

Let, after time 't', the concentration of oxygen be Lt

According to first order rate reaction, rate of the reaction is directly proportional to the concentration of reactant (here oxygen) left at that time(t).

$$-\frac{dL_t}{dt} \propto L_t \qquad \dots (1)$$

The negative sign (–) is indicating that along with time (t) the concentration of oxygen decreases.

We can rearrange the equation (1) as

$$-\frac{dL_t}{dt} = kL_t$$
; where, k = **De-oxygenation** constant/day

WORKED-OUT EXAMPLES -1

A 10.0 ml sample of sewage mixed with enough water to fill a 300ml bottle has an initial DO of 9.0 mg/L. To help assure an accurate test, it is desirable to have at least a 2.0mg/L drop in DO during the five days run, and the final DO should be at least 2.0 mg/L. For what range of BOD₅ would this dilution produce the desired result?

The dilution factor (P) =
$$\frac{10}{300}$$
 ... (1)

In the first case, drop of DO is 2mg/L i.e. the difference between initial DO and final DO is 2mg/L.

∴BOD₅ =
$$\frac{DO_i - DO_f}{P} = \frac{2}{10/300} \text{mg/L} = 60 \text{ mg/L}$$
 ... (2)

In the second case, final DO i.e. DO_f is 2mg/L.

∴BOD₅ =
$$\frac{DO_i - DO_f}{P} = \frac{9 - 2}{10/300} \text{mg/L} = 210 \text{mg/L}$$
 ... (3)

So, this dilution will be satisfactory for BOD₅ values between 60mg/L to 210mg/L.

WORKED-OUT EXAMPLES -2

The dilution factor P for an unseeded mixture of waste water is 0.030. The DO of the mixture is initially 9.0mg/L and after five days it has dropped to 3.0 mg/L. The reaction rate constant K has been found to be 0.22 / day at 20° C.

- (a) What is the BOD₅ of the waste?
- (b) What is ultimate carbonaceous BOD (BOD_u)?
- (c) What would be remaining oxygen demand after five days?
- (d) What would be the BOD₅ of the waste at 25° C?

(a)
$$BOD_5 = \frac{DO_i - DO_f}{P} = \frac{9 - 3}{0.030} = 200 \text{ mg/L}$$

(b) We know that, $BOD_t = L_0 (1-e^{-Kt})$

Where, $BOD_t = BOD$ of an waste water sample after time 't'

 L_0 = Total amount of oxygen needed to decompose the carbonaceous portion of the waste.

We can rearrange the above equation as $L_0 = \frac{BOD_t}{(1 - e^{-Kt})}$

$$or, L_0 = \frac{BOD_5}{(1 - e^{-K \times 5})} = \frac{200}{(1 - e^{-0.22 \times 5})} = 298.50 \text{ mg/L}$$

- (c) After five days, 200 mg/L of oxygen demand out of the total 300 mg/L would have already been used. The remaining oxygen demand would therefore be (298.50 200) mg/L = 98.50 mg/L.
- (d) At 25°C the BOD rate constant (K) would be

$$K_{25} = K_{20} \theta^{(T-20)}$$

or,
$$K_{25} = 0.22 \times (1.047)^{(25-20)}$$

or,
$$K_{25} = 0.277 / \text{day}$$

∴BOD₅ of that waste water at 25°C is

BOD₅ =
$$L_0$$
 (1-e^{-Kt})
= 300 (1-e^{-0.277×5})

$$BOD_5 = 203.57 \text{ mg/L}.$$