CIVIL ENGINEERING

Environmental Engg. : Vol-II

(Sewage Disposal & Air Pollution Engineering)

Comprehensive Theory
with Solved Examples *and* Practice Questions

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CHAPTER

1

Waste Water Characteristics

1.1 INTRODUCTION

In the past, the waste water from a community were not so much contaminated as they are today. The urbanisation, industrial growth and the improved standards of living, have increased the strength and quantity of muncipal sewage in recent years.

When untreated sewage is discharged into the river stream then, floating solids present in the sewage may come to the shore and create foul smells and bad odours. The large amount of organic matter present in sewage discharged into the river stream will consume the dissolved oxygen of the river stream, causing killing of fish and other undesirable effects. Hence, even though muncipal sewage contains 99.9% water, it requires treatment in order to avoid nuisance.

In this chapter, we will discuss about the various characteristics of sewage viz. physical, chemical, and biological characteristics. Also, we will study about the BOD (Biochemical oxygen demand), COD (Chemical oxygen demand), TOC (Total organic carbon) and their measurement techniques. Moreover, we will discuss about the permissible limit of the contaminants of waste water so that to perform desirable treatment processes in order to bring the quality of sewage to required level.

Important waste water contaminants

SL. No.	Contaminant	Source	Environmental Significance
1	Suspended Solids	Domestic use, Industrial wastes	Cause sludge deposits and anaerobic condition in aquatic environment
2	Biodegradable Organics	Domestic use, Industrial wastes	Cause biological degradation
3	Pathogens	Domestic water	Transmit communicable diseases
4	Nutrients	Domestic and Industrial waste	Cause eutrophication
5	Refractory Organics	Industrial waste	Cause taste and odour problems

1.2 CHARACTERISTICS OF SEWAGE

The quality of sewage can be checked and analysed by studying and testing its physical, chemical and bacteriological (biological) characteristics.

1.2.1 Physical Characteristics of Sewage and their Testing

The most important physical characteristics of waste water are

(i) Turbidity (ii) Colour (iii) Odour (iv) Temperature

(i) Turbidity: Sewage is normally turbid, resembling dirty dish water or waste water from baths having other floating matter like faecal matter, pieces of paper, cigarette-ends, match-sticks, greases, vegetable debris, fruit skins, soaps, etc. The turbidity increases as sewage becomes stronger.

Turbidity is measured photometrically by determining the percentage of light of a given intensity that is either absorbed or scattered. The degree of turbidity can be measured and tested by

(i) Turbidity rods (ii) Turbidimeters

It is expressed as the amount of suspended solids in mg/L or ppm (parts per million).

> **NOTE**
> (i) Turbidity rod consists of an aluminium rod which is graduated, as to give the turbidity in silica units.
> (ii) Turbidimeter works on the principle of measuring the interference caused by water sample to the passage of light rays.

(ii) Colour: The colour of sewage can normally be detected by the naked eye and it indicates the freshness of sewage. If colour is yellow, grey or light brown, it indicates fresh sewage and if the colour is black or dark brown it indicates stale or septic sewage. Some industrial waste water may also add colours to the domestic waste water. The common method used for removal of colour is coagulation followed by sedimentation.

> **NOTE:** When all the oxygen has disappeared from sewage, it becomes septic.

(iii) Odour: Although fresh sewage is odourless but in 3 to 4 hrs, the oxygen present in sewage vanishes making the sewage stale and septic. It starts causing odour of different gases especially hydrogen sulphide gas formed due to sewage decomposition.

The odour of wastewater is measured by **Threshold odour number (TON)** representing the extent of dilution required to make sample free from odour and is calculated as

$$\text{Threshold odour number (TON)} = \frac{V_s + V_D}{V_s}$$

where, V_s = Volume of sewage

V_D = Volume of distilled or odourless water added to just make sewage sample loss its odour.

> **NOTE:** Threshold odour number, represents the number of dilutions required to reduce an odour.

(iv) Temperature: Temperature of waste-water affects biological activity of bacteria in sewage and solubility of gases in sewage. It also affects the viscosity of sewage which, in turn affects sedimentation process in treatment. The temperature of sewage in our country is about 20°C ideal for biological activities.

1.2.2 Chemical Characteristic

Chemical characteristics are result of the solvent properties of water and they are often important in specifying waste water quality. Important chemical characteristics of waste water are listed below:

(a) Total solids, suspended solids and settleable solids
(b) pH value
(c) Chloride content
(d) Nitrogen content
(e) Presence of fats, greases and oils
(f) Sulphides, sulphates and H_2S gas
(g) Dissolved oxygen
(h) Chemical oxygen demand (COD)
(i) Theoretical oxygen demand (ThOD)
(j) Total organic carbon
(k) Bio-chemical oxygen demand (BOD)

(a) Total Solids, Suspended Solids and Settleable Solids

Solids present in sewage may be in any of the four forms, suspended solids, dissolved solids, colloidal solids and settleable solids. Suspended solids are those solids which remain floating in sewage. Dissolved solids are those which remain dissolved in waste water just as salt in water. Colloidal solids are finely divided solids remaining either in solution or in suspension. Settleable solids are that portion of solid matter which settles out, if the waste water is allowed to remain undisturbed for a period of 2 hours.

NOTE It has been estimated that about 1000 kg of sewage contains about 0.45 kg of total solids, out of which 0.225 kg is in solution, 0.112 kg is in suspension and 0.112 kg is settleable. The solids in sewage comprise of both: the organic and inorganic solids, which is about 45 and 55 percent of total solids respectively.

- Inorganic matter consist of sand, gravel, debris, chlorides, sulphates etc.
- Organic matter consist of
  - Carbohydrates such as cellulose, cotton, fibre, sugar etc.
  - Fats and oils from kitchen, garages, shops etc.
  - Nitrogenous compounds like proteins, urea, fatty acids etc.

It is to be noted that in general, presence of inorganic solids in waste water is not harmful and they can be removed by mechanical appliances. However, organic solids whether suspended or dissolved can cause nuisance if they are disposed off without treatment. The amount of various solids present in waste water can be determined as follows:

The amounts of various kinds of solids present in waste water can be determined as follows:

(a) The difference between the total solids (S_1) and the suspended solids (S_2) represent dissolved solids plus colloidals or filterable solids (S_3)

i.e. $S_3 = S_1 - S_2$.

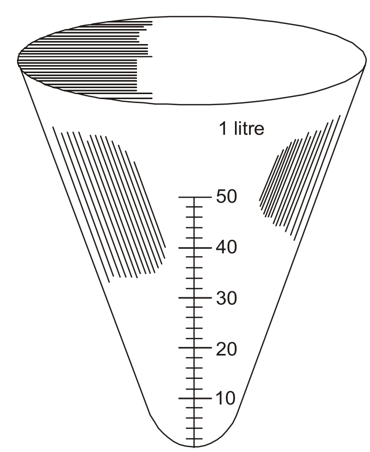


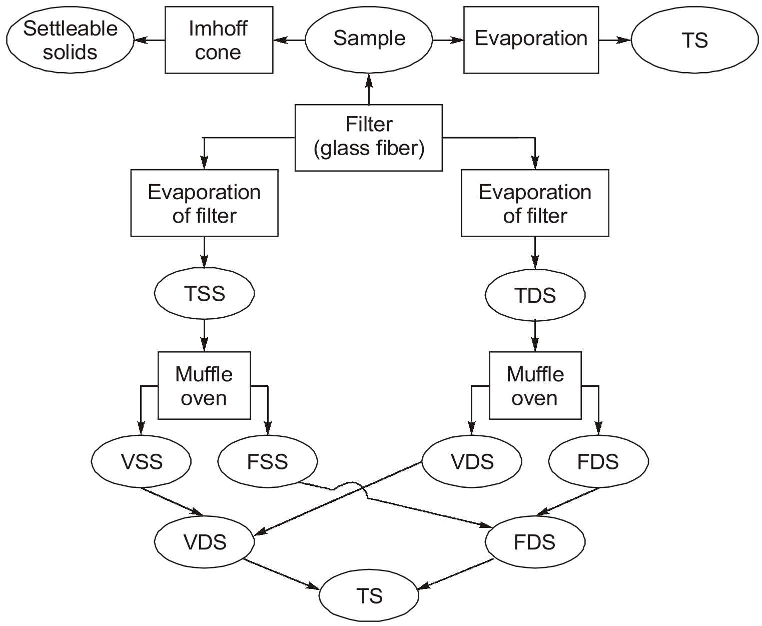
Fig. Imhoff cone (Conical Glass Vessel)

(b) As we know that total suspended solids(S_2) can be either volatile or fixed. If their proportion is to be determined, then the suspended solids (S_2) in step (b) is burnt and ignited at about 550°C in an electro furnace for about 15 to 20 minutes. Loss of weight will represent the amount of volatile solids in volume of sample filtered through filter. Let, the volatile suspended solid concentration by S_4(in mg/l).

(c) Now, fixed suspended solid concentration (S_5) can be calculated as, $S_5 = S_2 - S_4$.

(d) The quantity of settleable solids (S_6) can be determined with the help of a specially designed conical glass vessel known as Imhoff cone as shown in figure. In this cone, sewage is allowed to stand for about 2 hours and quantity of solids settled in bottom of cone represents the quantity of settleable solids.

For better understanding of complete process, flow-chart shown in figure below can be referred:



TS = total solids
TSS = total suspended solids
TDS = total dissolved solids
VSS = volatile suspended solids
FSS = fixed suspended solids
VDS = volatile dissolved solids
FDS = fixed dissolved solids
TVS = total volatile solids
TFS = total fixed solids

(b) pH Value

The pH value of sewage indicates the negative log of hydrogen ions concentration present in sewage.

i.e. $pH = -\log H^{+}$ or $H^{+} = (10)^{-pH}$

It indicates the extent of alkalinity in sewage. The determination of pH value is very important, as it gives an idea about certain treatments which depends upon pH value. The pH value can be measured by the help of potentiometer which measure the electrical potential exerted by the hydrogen ions, and thus indicating their concentration.

> **NOTE** The fresh sewage is generally alkaline in nature (with pH more the 7) but as time passes its pH tends to fall due to production of acids by bacterial action in anaerobic or nitrification processes.

(c) Chloride Content

Chlorides are generally present in municipal sewage and are derived from the kitchen wastes, human faeces and urinary discharge etc. The normal chloride content of domestic sewage is 120 mg/*l*, however, large amount of chlorides may enter from industries like ice-cream plants, meat salting etc. thus increasing the chloride content of waste water. The chloride content can be measured by titrating the waste water with standard silver nitrate solution, using potassium chromate as an indicator.

(d) Nitrogen Content

The presence of nitrogen in sewage indicates the presence of organic matter and may occur in one or more of the following forms:

(i) Free ammonia called ammonia nitrogen (indicates recent pollution).

(ii) Albuminoid nitrogen called organic nitrogen (indicates quantity of nitrogen before decomposition has started).

(iii) Nitrites (indicates partly decomposed condition).

(iv) Nitrates (indicates old pollution (fully oxidised)).

NOTE: Lack of nitrates causes the body to turn bluish, it may lead the child to turn blue. Hence, this disease, popularly called blue baby disease or mathemoglobinemia.

(e) Presence of Fats, Oils and Greases

Greases, fats and oils are derived in sewage from the discharge of animals and vegetable matter or from industries like garages, kitchen of hotels and restaurants etc. Such matter form scum on the top of the sedimentation tanks and clog the voids of the filtering media. Therefore, they interfere with the normal treatment methods, and hence need proper detection and removal. Fats and oils are compounds of alcohol or glycerol with fatty acids.

The amount of fats and greases in a sewage sample is determined by the fact that these are soluble in ether and when either is evaporated, it leaves their-soluble matter representing quantities of fats and oils. Thus, a sample of sewage is evaporated and residual solids left are then mixed with ether-solution is now poured off leaving behind fats and grass as a residue which can be weighed.

(f) Sulphides, Sulphates and Hydrogen Sulphide Gas

Sulphides and sulphates are formed due to the decomposition of various sulphur containing substances present in sewage. This decomposition also leads to evolution of hydrogen sulphide gas, causing bad smells and odours, besides causing corrosion of concrete sewer pipes.

In aerobic digestion of sewage, aerobic and facultative bacteria oxidise sulphur and its compound to initially form sulphides. These sulphides ultimately break down to form sulphate ions (SO_4^{2-}) which is a stable and an unobjectionable end product.

In anaerobic digestion of sewage, anerobic and facultative bacteria reduce sulphur and its compounds into sulphides, with evolution of H_2S gas along with methane and carbon dioxide causing very obnoxious odour.

(g) Dissolved Oxygen (D.O)

Dissolved oxygen present in sewage is very important for respiration of aerobic micro-organism as well as for all other aerobic life forms. Quantity of D.O. indicates the freshness of sewage. The dissolved oxygen in fresh sewage depends upon temperature. If the temperature of sewage is more, the D.O. content will be less. Maximum quantity of D.O. that can remain mixed in water at a particular temperature is called **Saturation Dissolved Oxygen.** The D.O. content of sewage is generally determined by the **Winkler's Method** which can be described as follows:

- Collect a water sample in a clean glass bottle and add 1 ml of $MnSO_4$ solution per litre of sample. This helps to oxidise any organic matter in the sample, which can interface with the oxygen measurement.
- Add 1 ml of alkaline iodide – azide reagent per litre of sample and mix thoroughly. This reacts with any dissolved oxygen in the sample, converting it to iodide ions.
- Add 1 ml of concentrated H_2SO_4 per litre of sample, taking care to avoid splashing. This reacts with the iodide ions to produce iodine.
- Allow the solution to stand for at least 10 minutes to allow the iodine to fully develop. The solution turns yellow-brown.
- Add 1 ml of starch solution per litre of sample, and mix throughly. This will cause the solution to turn blue-black.

- Titrate the solution with adding $Na_2S_2O_3$ solution drop by drop until the blue-black colour disappears. This indicates that all of the iodine has been reacted with the thiosulphate.
- Volume of thiosulphate used represents the amount of oxygen that was originally present in the water sample.

NOTE

- Water is first mixed with manganese sulphate ($MnSO_4$) and alkali-iodide – Azide reagent is added. If white precipitate is formed, dissolved oxygen (DO) is absent and, if brown precipitate is formed, it means DO is present.

  Sample + $MnSO_4$ + NaoH + kI + NaN_3 $\rightarrow$ $Mn(OH)_2$ (White PPt) DO is absent.

  Sample + $MnSO_4$ + NaoH + kI + NaN_3 $\rightarrow$ MnO_2 (Brown PPt) DO is present.
- The solubility of oxygen in sewage is 95% of that in distilled water.
- It is necessary to ensure at least 4 ppm of dissolved oxygen in discharged treated sewage, otherwise fish are likely to be killed.
- Dissolved oxygen is desirable in drinking water but it is usually removed from boiler feed waters because of the manner in which it accelerates corrosion of metals.

(h) Chemical Oxygen Demand (COD) and Theoretical oxygen demand (THOD)

As discussed earlier, wastewater contains organic and inorganic matter depending upon its source and characteristics etc. Organic matter is most often assessed in terms of oxygen required to completely oxidise organic mater to CO_2, H_2O and other oxidised species.

Now, determination of oxygen required to completely oxidise the organic matter can be theoretically done if concentration and chemical formulas of organic matter present in waste water are known. This oxygen requirement for oxidation of organic matter which can be computed by writing the balanced equation for organic matter is known as theoretical oxygen demand (ThoD).

However, as it is impossible to known about the chemical composition of organic matter, another test known as chemical oxygen demand (COD) is used to express the organic content of waste-water. COD test is used to measure content of organic matter of waste water, both biodegradable and non-biodegradable. It measures oxygen equivalence of organic matter in wastewater that can be oxidised chemically using dichromate in an acid solution as illustrated in following equation given below:

$$C_nH_aO_bN_C + dCr_2O_7^{2-} + (8d + C)H^+ \rightarrow nCO_2 + \frac{a + 8d - 3CH_2O}{2} + cNH_4^+ + 2dCr^{3+}$$

where, $$d = \frac{2n}{3} + \frac{a}{6} - \frac{b}{3} - \frac{c}{2}$$

NOTE

- COD test is also called dischromate oxygen demand test.
  In order to perform this test, a known quantity of waste-water is mixed with a known quantity of standard solution of potassium dischromate and mixture is heated. The organic matter is oxidised by $k_2Cr_2O_7$ (in presence of H_2SO_4). The resulting solution of $k_2Cr_2O_7$ is titrated, and oxygen used in oxidising waste water is determined.
- In this test an acid like H_2SO_4 helps to break down the complex molecules.

(i) Total organic carbon

It is an another important method of expressing organic matter in terms of its carbon content. As the carbon is the primary constituents of organic matter, therefore the chemical formula of every organic compound will reflect the extent of carbon present in that compound. Known concentrations of such chemical compounds in a given waste water will thus enable us to theoretically calculate the carbon present in that waste water.

(j) Bio-Chemical oxygen demand

Organic matter present in waste-water can be of two types:

(i) Biologically active or biologically degradable i.e. matter which can be biologically oxidised.

(ii) Biologically inactive matter that can not be biologically oxidised.

It is to be noted that only biologically active organic matter is point of interest for us while the COD test gives us total organic matter i.e. biologically active and inactive both. Hence, another oxygen demand of waste-water known as Biochemical oxygen demand (BOD) is determined to know the amount of biologically active organic matter present in sewage.

NOTE: Generally, ThOD > COD > BOD > TOC

1.3 DETERMINATION OF BOD

Presence of sufficient oxygen in sewage ensures that the process of aerobic biological decomposition of organic matter will continue until all the matter is consumed. In this process, basically three activities are supposed to occur as follows:

(i) A portion of organic matter is oxidised to end products in order to obtain energy for cell maintenance and synthesis of new cell tissue. Chemical reaction for this activity can be represented as given below:

$$COHNS + O_2 + \text{bacteria} \rightarrow CO_2 + H_2O + NH_3 + \text{Other end product} + \text{energy} \quad \text{...(i)}$$

where, COHNS represents elements of organic matter i.e. carbon, oxygen, hydrogen, nitrogen and sulphur.

(ii) Some part of organic matter is converted into new cell tissue using part of energy released during oxidation in above activity. Chemical reaction for this activity can be represented as given below:

$$COHNS + O_2 + \text{bacteria} + \text{Energy} \rightarrow C_5H_7NO_2 \quad \text{...(ii)}$$

where $C_5H_7NO_2$ is the term used to represent new cell tissue.

(iii) Finally, when the organic matter is used up, the new cell begins to consume their own cell tissue to obtain energy for cell maintenance and this activity is known as **endogenous respiration**. Chemical reaction for this activity can be represented as given below:

$$C_5H_7NO_2 + 5O_2 \rightarrow 5CO_2 + NH_3 + 2H_2O$$

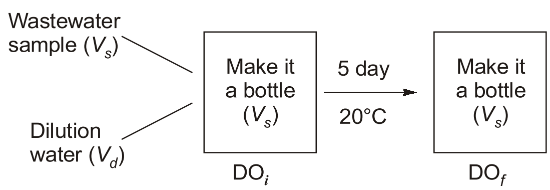
If only oxidation of organic carbon present in waste water is considered, to complete all the above three reactions. It is also known as first-stage BOD, and is usually denoted by L_0. BOD of waste water depends upon time and it is in general practice to adopt 5-day BOD as standard BOD. 5-day BOD of water is denoted by BOD_5 or simply BOD. It is about 68% of ultimate BOD.

Procedure

1. A standard bottle (generally 300 ml volume) is filled with wastewater sample. Let the volume of sample and bottle is V_s and V_b respectively.

2. After filling the wastewater sample in bottle, it is filled with dilution water saturated in oxygen and containing the nutrients required for biological growth. Let, the volume of dilution water added is V_d. Here, the sum of the volume of waste water sample (V_s) and volume of dilution water (V_d) must be equal to volume of BOD bottle(V_b).
3. Now, dissolved oxygen of mix of sample and dilution water is measured. Let, DO of mix is DO_i. After finding DO_i, bottle is incubated for 5 days at 20°C.
4. After 5 days, dissolved oxygen (DO) of mix is given measured. Let, it is represented by DO_f.

   It is to be noted that temperature should remain constant during the period of incubation.



- The volume of waste water sample taken depends on the acidity of the waste water sample.
  Now,

As we know,

$$BOD_{mix} = \frac{BOD_{sample} \times Vol_{sample} + BOD_{D/W} \times Vol_{D/w}}{Vol_{sample} + Vol_{D/w}}$$

where,

BOD_{mix} = BOD of (i.e. BOD of wastewater sample and dilution water)
= $(DO_i - DO_f)$ [∵ BOD is dissolved oxygen consumed]
$BOD_{D/W}$ = BOD of dilution water
= 0 [Organic matter in dilution water is zero]
Vol_{sample} = Volume of wastewater sample BOD bottle = V_s
$Vol_{D/W}$ = Volume of dilution water in BOD bottle = V_d

So, putting values we get

$$(DO_i - DO_f) = \frac{BOD_{sample} \times V_s + 0 \times V_d}{V_s + V_d} \quad \text{...(ii)}$$

Rearranging (ii), we get

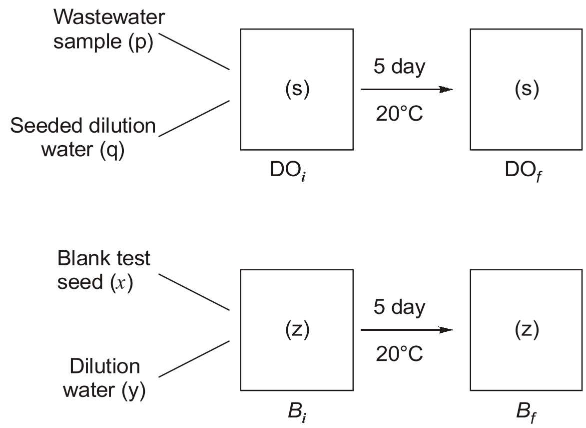
$$BOD_{sample} = (DO_i - DO_f) \times \frac{V_s + V_d}{V_s}$$
$$= (DO_i - DO_f) \times \text{Dilution factor}$$

Dilution factor is defined as ratio of volume of diluted sample and volume of undiluted sewage sample.

> NOTE: Dilution water is added to sample to maintain sufficient supply of oxygen for aerobic microbes to oxidise organic matter.

Special case: When wastewater sample is very acidic.

If the waste water sample is very acidic, then the number of aerobic microbes is inadequate, so the procedure discussed above will not give accurate results. In this case, seeded water is added to wastewater sample in place of dilution water. A seeded water is one in which population of aerobic microbes has been already added. Also, 5 day BOD of seeded water is also determined by the procedure discussed above. The complete procedure can be understood with the figure given below:



In figure B_i and B_f represents the DO content of mix of seeded water and dilution water before and after incubation.

Now, BOD of seed dilution water is,

$$\text{BOD}_{\text{s/w}} = (B_i - Bf) \times \frac{z}{x} \qquad \text{...(i)}$$

where, z is volume of mix of seed and dilution water,

x is volume of seed added in blank test.

Again, $$\text{BOD}_{\text{mix}} = \frac{\text{BOD}_{\text{sample}} \times V_{\text{sample}} + \text{BOD}_{s/w} + \text{Vol}_{s/w}}{V_{\text{sample}} + \text{Vol}_{s/w}}$$

where, BOD_{mix} = BOD of mix of wastewater sample and seeded water

$= (\text{DO}_{\text{i}} - \text{DO}_{\text{f}})$

$\text{BOD}_{\text{Sample}}$ = BOD of seeded dilution water calculated by eq. (i)

$\text{Vol}_{\text{Sample}}$ = Volume of wastewater sample

$= p$

$Vol_{\text{s/w}}$ = Volume of seeded dilution water $= q$

$$(\text{DO}_{\text{i}} - \text{DO}_{\text{f}}) = \frac{\text{BOD}_{\text{sample}} \times p + \text{BOD}_{s/w} + q}{p+q} \qquad \text{...(iii)}$$

Rearranging (iii), we get

$$\frac{[(\text{DO}_i - \text{DO}_f) \times (p+q)] - [\text{BOD}_{s/w} \times q]}{p} = \text{BOD}_{\text{Sample}} \qquad \text{...(iv)}$$

Now, $p + q$ = Volume of bottle

$= s$

Putting (i) in (iv)

$$\text{BOD}_{\text{Sample}} = \frac{(\text{DO}_i - \text{DO}_f) \times s - (Bi - B_f) \times \frac{z \times q}{x}}{p} \qquad \text{...(v)}$$

$$= \left[(\text{DO}_i - \text{DO}_f) - (B_i - B_f) \times \frac{z}{x} \times \frac{q}{s}\right] \times \frac{s}{p}$$

Generally, $s = z$ [Both are BOD bottle]

Simplifying

$$\text{BOD}_{\text{Sample}} = \left[(\text{DO}_i - \text{DO}_f) - (B_i - B_f) \times \frac{q}{x}\right] \times \frac{s}{p}$$

$$= \left[(\text{DO}_i - \text{DO}_f) - (B_i - B_f) f\right] \times \text{Dilution factor}$$

where, f is the ratio of volume of seeded dilution water (or seed in diluted sample) to volume of seed in blank sample.

If $q = x$,

$$\text{BOD}_{\text{sample}} = [(DO_i - DO_f) - (B_i - B_f)] \times \text{Dilution factor}$$

1.4 BOD-CURVE

As discussed earlier, oxygen is used up by bacterias to oxidise organic matter, to synthesis new cells and in endogenous respiration. Total oxygen demand of waste water is exerted by three class of materials:

(a) Carbonaceous organic matter.

(b) Nitrogenous organic matter.

(c) Chemical reducing compounds e.g. Fe^{2+}, SO_3^{2-}, S^{2-}, which are oxidised by dissolved oxygen.

NOTE: For domestic sewage, nearly all oxygen demand is due to carbonaceous organic matter.

Nitrogenous organic matter such as ammonia is produced during hydrolysis of proteins. Some types of bacterias first oxidise ammonia to nitrite and then to nitrate. The generalized reaction are as follows:

Conversion of ammonia to + nitrite (by Nitrosomnas bacteria)

$$NH_3 + \frac{3}{2}O_2 \rightarrow NHO_2 + H_2O$$

Conversion of nitrite to nitrate (by nitrobacter bacteria)

$$HNO_2 + \frac{1}{2}O_2 \rightarrow HNO_3$$

1.4.1 Overall conversion of ammonia to nitrate

The chemical reaction associated with the overall conversion of ammonia to nitrate are as below:

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

The oxygen demand associated with oxidation of ammonia to nitrate is called the **nitrogenous biochemical oxygen demand (N – BOD)**. As the reproductive rate of nitrifying bacteria is slow, therefore oxygen demand of carbonaceous organic matter is first fulfilled followed by nitrogenous organic matter.

BOD corresponding to carbonaceous and nitrogenous organic matter is represented by Ist stage BOD and IInd stage BOD respectively as shown by curve below:

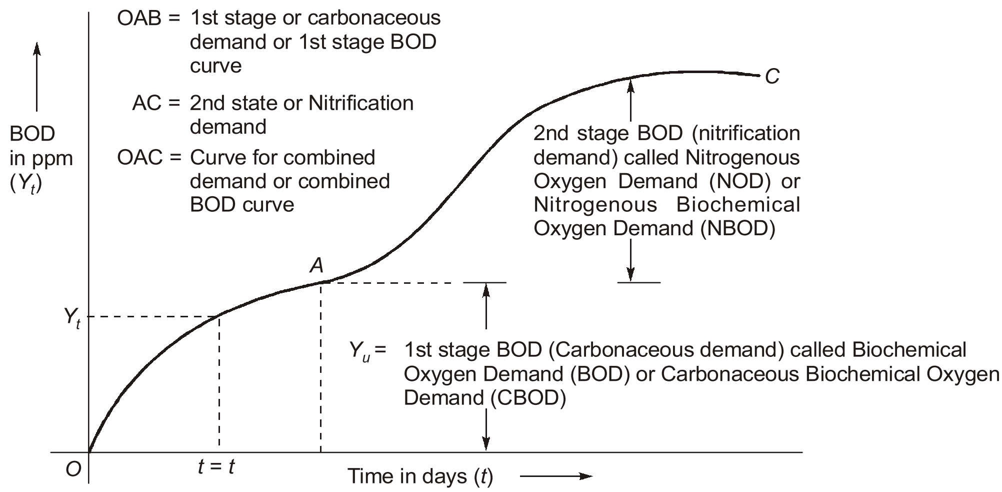


Fig. Different BOD stages with time

The portion OA and AC of curve shows the carbonaceous and nitrogenous BOD respectively.

1.4.2 Reaction Kinetics

The rate of BOD exertion is modeled based on assumption that amount of organic matter remaining at any time t is governed by **first order kinetics** as given below:

$$\frac{dL_t}{dt} = -kL_t \quad \text{...(i)}$$

where, k = Rate constant signifying rate of oxidation organic matter depending upon nature of organize

L_t = Oxygen equivalent of Carbonaceous oxidisable organic matter present oxidation in (mg/l)

On rearranging and integrating (i), we get

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

$$\Rightarrow l_n[L_t] = -kt + C \quad \text{...(ii)}$$

Now, at $t = 0$,

L_t = Total carbonaceous matter at the starting of oxidation

Now, at $t = 0$

L_t = Ultimate BOD(L_0)

Putting boundary condition in (ii),

$$\Rightarrow l_n[L_0] = -k_n L_0$$

Putting value of C in eq. (ii)

$$\Rightarrow l_n[L_t] = -kt + l_n[L_0]$$

$$\Rightarrow \frac{L_t}{L_0} = e^{-kt}$$

$$\Rightarrow L_t = L_0 e^{-kt} \quad \text{...(iii)}$$

$$\Rightarrow \frac{L_t}{L_0} = e^{-kt}$$

$$\Rightarrow \qquad L_t = L_0 e^{-kt} \qquad \text{...(iii)}$$

In eq. (iii), L_t represents the remaining carbonaceous organic matter or remaining BOD after t days from start of oxidation.

Now, BOD exerted upto t days, $(BOD)_t$ = Ultimate BOD-Remaining BOD after t days

$$= L_0 - L_t = L_0 - L_0 e^{-kt} \qquad [\because L_t = L_0 e^{-kt}]$$

$$= L_0(1 - e^{-kt}) \qquad \text{...(iv)}$$

Also, $$BOD_t = L_0(1 - 10^{-k_D t}) \qquad \text{...(v)}$$

where, $$k_D = k/2.303 = 0.434\ K$$

k_D is known as deoxygenation constant. k_D determines the rate of BOD reaction, without influencing the ultimate BOD. It is found to vary with temperature of sewage and this relationship is given by the equation:

$$k_{D(T°C)} = k_{D(20°)}(1.047)^{T-20°} \qquad [\text{When } T > 20°C] \qquad \text{...(vi)}$$

$$k_{D(T°C)} = k_{D(20°)}(1.056)^{T-20°} \qquad [\text{When } T < 20°C] \qquad \text{...(vii)}$$

Value of k_D depends upon nature of organic matter present in sewage. Simple compounds such a sugars and starches are easily decomposed by micro-organism and have high k_D rate, while complex molecules such as phenols are difficult to assimilate and have low k_D values. Some typical values of k_D are given in table.

Typical Values of K_D at 20°C for Various Types of Waters and Waste water

Water Type	K_D value per day
Tap waters	< 0.05
Surface waters	0.05 – 0.1
Municipal wastewaters	0.1 – 0.15
Treated sewage effluents	0.05 – 0.1

As the temperature increases, value to k_D increases due to which rate of reaction increases and in turn rate of BOD exertion also increases as depicted by figure.

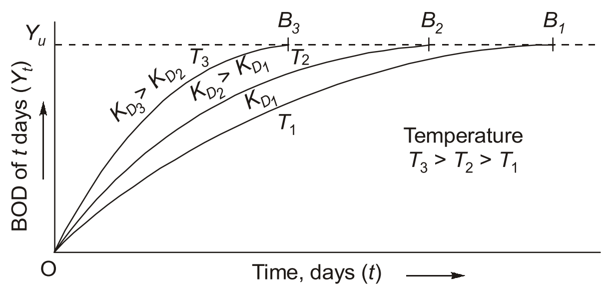


Fig. BOD exertion as a function of K_D

1.4.3 Laboratory estimation of k_D and L_0 by Thomas's graphical method

Value of k_D can be computed from BOD values measured at various time duration (in days). The sewage samples are tested for BOD at different time duration. A graph is now plotted between value of function

$$\sqrt[3]{\frac{t\,(\text{in days})}{y_t \text{ i.e.BOD (in mg/}l)}}$$ on y-axis and time t on x-axis as shown in figure.

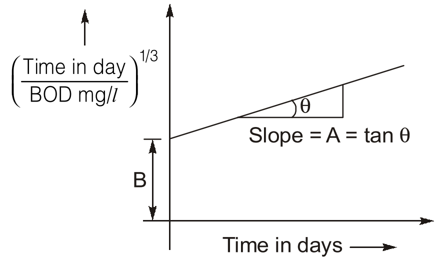


Fig. Relation between K_D and Time (in days)

$$k_D = \frac{2.61A}{B}$$

Where,
A = Slope of line
B = Intercept of line on y-axis.

Also, Ultimate BOD, $L_0 = \frac{1}{2.3k_D B^3}$

NOTE: BOD exerted upto time t given be eq. (v) corresponds to only 1st stage BOD.

Example 1.1 For a waste, the 5-day BOD at 20°C is found to be 200 mg/L. For the same waste, 5-day BOD at 30°C will be

(a) less than 200 mg/L
(b) more than 200 mg/L
(c) 200 mg/L
(d) zero, as the bacteria cannot withstand such a high temperature

Ans. (b)

The effect of temperature on BOD can be approximately given by the Van't Hoff-Arrhenius models:

$$K_T = K_{20}(1.047)^{T-20}$$

At $T = 30°C,\ K_T > K_{20}$

$$BOD_{5,30°C} = L_0\left(1 - e^{-K_T t}\right)$$

$\therefore$ $BOD_{5,30°C} > BOD_{5,20°C}$

Example 1.2 The ultimate BOD value of a waste

(a) increases with temperature
(b) decreases with temperature
(c) remains the same at all temperatures
(d) doubles with every 10°C rise in temperature

Ans. (c)

Ultimate BOD represents the biodegradable organic matter, so it will remain unchanged.

Example 1.3 For a waste water the BOD_5 at 20° is found to be 200 mg/l. For same waste BOD_3 at 30°C will be? The reaction constant 'K' (to the base e) is 0.2 per day.

Solution:

$$BOD_5 \text{ at } 20°C = L_0[1 - e^{-K \times 5}]$$

$$\text{BOD}_3 \text{ at } 30°\text{C} = L_0[1 - e^{-K' \times 3}]$$

$$L_0 = \text{BOD}_u \quad \text{(Remain constant)}$$

$$200 = L_0[1 - e^{-5K}] \quad \text{...(i)}$$

$$\text{BOD}_3 = L_0[1 - e^{-3K'}] \quad \text{...(ii)}$$

From (i) and (ii)

$$\frac{200}{1-e^{-5K}} = \frac{\text{BOD}_3}{1-e^{-3K'}} \Rightarrow \frac{1-e^{-3K'}}{1-e^{-5K}} = \frac{\text{BOD}_3}{200}$$

But,

$$K' = K(1.047)^{30-20} = 0.2[1.047]^{10} = 0.316$$

$$\Rightarrow \quad \text{BOD}_3 = 200\left[\frac{1-e^{-3\times0.316}}{1-e^{-5\times0.2}}\right] = \frac{0.6125}{0.632} \times 200 = \mathbf{193.78\ mg/}\boldsymbol{l}$$

EXAMPLE : 1.4

Data from an unseeded domestic waste water BOD test are : 5 m*l* of waste in 300 m*l* bottle, initial D.O. of 7.8 mg/*l*, and 5 days DO equal to 4.3 mg/*l*. Compute

(a) the BOD; and

(b) the ultimate BOD, assuming a k_D of 0.10 day^{-1}

Solution:

(a) Initial D.O. = 7.8 mg/*l*

D.O. after 5 days of incubation =4.3 mg/*l*

∴ D.O. consumed in 5 days = 7.8 – 4.3 = 3.5 mg/*l*

$$\text{BOD}_5 \text{ of wastewater} = \text{D.O consumed by diluted sample} \times \left[\frac{\text{vol. of diluted sample}}{\text{vol. of undiluted sewage used}}\right]$$

$$= 3.5 \text{ mg}/l \times \left[\frac{300 \text{ m}l}{5 \text{ m}l}\right] = 210 \text{ mg}/l$$

(b) Now, using equation $Y_t = L\left(1-(10)^{-K_D \cdot t}\right)$, we have

$$Y_5 = L\left(1-(10)^{-K_D \cdot 5}\right)$$

where, K_D = 0.1 per day and Y_5 = 210 mg/*l*

$$\therefore \quad 210 = L\left[1-(10)^{-0.1\times5}\right] = L\left[1-\frac{1}{(10)^{0.5}}\right]$$

$$= L[1 - 0.316] = 0.684\, L$$

or

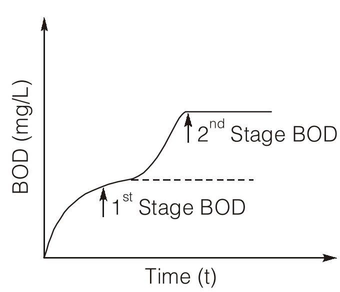
$$L = \frac{210}{0.684} \text{mg}/l = \mathbf{307.1\ mg/}\boldsymbol{l}$$

OBJECTIVE BRAIN TEASERS

Q.1 An industrial waste water enters a stream having a BOD concentration of 10 mg/L and a flow of 20 m^3/s. If the flow of wastewater is 1.5 m^3/s and its BOD concentration is 250 mg/L, then the BOD concentration in the stream at a point downstream of the point of confluence of wastewater with the stream will be
(a) 2.67 mg/L (b) 12.09 mg/L
(c) 13.00 mg/L (d) 26.74 mg/L

Q.2 The following data pertain to a sewage sample:
Initial DO = 10 mg/L
Final DO = 2 mg/L
Dilution to 1%
The BOD of the given sewage sample is
(a) 8 mg/L (b) 10 mg/L
(c) 100 mg/L (d) 800 mg/L

Q.3 The second stage BOD as shown in the figure is due to



(a) experimental error
(b) increased activity of bacteria
(c) nitrification demand
(d) interference by certain chemical reactions

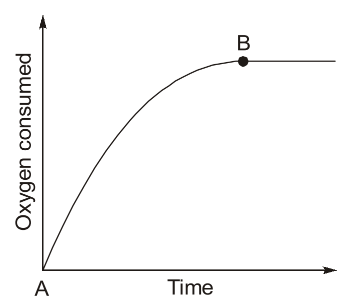
Q.4 If the BOD_3 of a wastewater sample is 75 mg/L and reaction rate constant k (base e) is 0.345 per day, the amount of BOD remaining in the given sample after 10 days is
(a) 3.12 mg/L (b) 3.45 mg/L
(c) 3.69 mg/L (d) 3.92 mg/L

Q.5 Which one of the following pairs is not correctly matched?
(a) BOD/COD = 0 : Waste-water is toxic
(b) BOD/COD ≤ 0.2 : Acclimatization of seed is necessary
(c) BOD/COD ≥ 0.6 : Waste-water is non-biodegradable
(d) BOD = COD = 0 : Waste-water is devoid of organic matter

Q.6 What is 5 days 20°C BOD equal to?
(a) 3 days 27°C BOD
(b) 4 days 30°C BOD
(c) 6 days 32°C BOD
(d) 7 days 35°C BOD

Q.7 In context of water polluted with sewage, what does BOD signify?
(a) Biological oxygen demand
(b) Bacteriological oxygen demand
(c) Biochemical oxygen demand
(d) Biology of degradation

Q.8 The figure below shows, BOD curve when the experiment was conducted at 20°C. If the experiment is conducted at 30°C, then the portion AB of the curve



(a) shifts to the left
(b) shifts to the right
(c) remains unchanged
(d) shrinks

Q.9 In aerobic environment, nitrosomonas convert
(a) NH_3 to NO_2^- (b) NO_2^- to NO_3^-
(c) NH_3 to N_2O^- (d) NO_2^- to HNO_3

Q.10 A sample of sewage is estimated to have a 5 day 20° C BOD of 250 mg/l. If the test temperature be 30°C, in how many days will the same value of BOD be obtained?
(a) 1.5 days (b) 2.5 days
(c) 3.3 days (d) 7.5 days

Q.21 **List-I** contains some properties of water/waste water and **List-II** contains list of some tests on water/ waste water. Match **List-I** with **List-II** and select the correct answer using the codes given below the lists:

List-I

A. Suspended solids concentration
B. Metabolism of biodegradable organics
C. Bacterial concentration
D. Coagulant dose

List-II

1. BOD
2. MPN
3. Jar test
4. Turbidity

Codes:

	A	B	C	D
(a)	2	1	4	3
(b)	4	1	2	3
(c)	2	4	1	3
(d)	4	2	1	3

Q.22 To determine the BOD_5 of a waste water sample, 5, 10 and 50 mL aliquots of the waste water were diluted to 300 mL and incubated at 20°C in BOD bottles for 5 days. The results were as follows:

S.No.	Waste-water volume, mL	Initial DO, mg/L	DO after 5 days, mg/L
1.	5	9.2	6.9
2.	10	9.1	4.4
3.	50	8.4	0.0

Based on the data, the average BOD_5 of the waste water is equal to

(a) 139.5 mg/L (b) 126.5 mg/L
(c) 109.8 mg/L (d) 72.2 mg/L

ANSWER KEY

1. (d)	2. (d)	3. (c)	4. (c)	5. (c)
6. (a)	7. (c)	8. (a)	9. (a)	10. (c)
11. (c)	12. (c)	13. (b)	14. (c)	15. (b)
16. (c)	17. (128)	18. (d)	19. (c)	20. (d)
21. (b)	22. (a)			

HINTS & EXPLANATIONS

1. (d)

$$BOD_{stream} = \frac{Q_1y_1 + Q_2y_2}{Q_1 + Q_2}$$

$$= \frac{20 \times 10 + 1.5 \times 250}{20 + 1.5}$$

$$= \mathbf{26.74\ mg/L}$$

2. (d)

BOD = [Initial DO – Final DO] × Dilution Factor

Where Dilution Factor

$$= \frac{\text{Volume of diluted sample}}{\text{Volume of undiluted sample}}$$

$$= (10 - 2) \times \frac{100}{1} = \mathbf{800\ mg/L}$$

4. (c)

The BOD at any instant is given by

$$L_t = L(1 - e^{-kt})$$

$$\Rightarrow \quad 75 = L(1 - e^{-0.345 \times 3})$$

$$\Rightarrow \quad L = \frac{75}{1 - 0.355} = 116.32\text{ mg/L}$$

BOD after 10 days,

$$L_{10} = L(1 - e^{-0.345 \times 10})$$

$$= 116.32 \times 0.968 = 112.63\text{ mg/L}$$

Amount of BOD remaining $= L - L_{10}$

$$= 116.32 - 112.63 = 3.69\text{ mg/L}$$

5. (c)

$BOD_5/COD \geq 0.6$ means waste water is biodegradable

6. (a)

$$BOD_t = L_0 (1 - e^{-kt})$$

and $k_T = k_{20}(1.047)^{T-20}$

BOD_5 at 20°C will be equal to a BOD_t for given temperature when $k_T t$ is equal to $k_{20} \times 5$.

$$k_T t = k_{20} \times 5$$

or

$$\frac{k_T}{k_{20}} = \frac{5}{t} = (1.047)^{T-20}$$

$$Y_1 = 180 \text{ mg/L}$$
$$Y_2 = 180 \text{ mg/L}$$
$$L_{0_1} = \text{ultimate BOD} = L_{02}$$
$$t_2 = 2.5 \text{ days}$$
$$k_{D_2} = ?$$

$$\because \quad \frac{Y_1}{Y_2} = \frac{1-10^{-k_{D_1} t_1}}{1-10^{-k_{D_2} t_2}}$$

$$\Rightarrow \quad \frac{180}{180} = \frac{1-10^{-0.0781\times 5}}{1-10^{-k_{D_2}\times 2.5}}$$

$$\Rightarrow \quad 10^{2.5k_{D_2}} = 10^{0.3906}$$

$$\Rightarrow \quad k_{D_2} = \frac{0.3906}{2.5} = 0.15624$$

Now $k_{D_2} = k_{D_1}[1.047]^{T-20}$

$$\Rightarrow \quad 0.15624 = 0.434 \times 0.18\,[1.047]^{T-20}$$

$$\Rightarrow \quad 2 = [1.047]^{T-20}$$

$$\Rightarrow \quad \log 2 = (T-20)\log 1.047$$

$$\Rightarrow \quad T = \mathbf{35.09°C}$$

22. (a)

BOD in mg/L = [Initial *DO* – Final *DO*] × dilution factor

$$[\text{BOD}_5]_1 = (9.2-6.9)\times\frac{300}{5} = 138 \text{ mg/L}$$

$$[\text{BOD}_5]_2 = (9.1-4.4)\times\frac{300}{10} = 141 \text{ mg/L}$$

As final DO and 3rd sample is zero, hence the sample is discarded.

$$\text{Average}\,\text{BOD}_5 = \frac{138+141}{2}$$
$$= \mathbf{139.5 \text{ mg/L}}$$

CONVENTIONAL BRAIN TEASERS

Q.1 The following observations were made on a 3% dilution of waste water.

Dissolved oxygen (*D.O.*) of aerated water used for dilution = 3.0 mg/*l*

Dissolved oxygen (*D.O.*) of diluted sample after 5 days incubation = 0.8 mg/*l*

Dissolved oxygen (*D.O.*) of original sample = 0.6 mg/*l*

Calculate the B.O.D. of 5 days and ultimate BOD of the sample assuming that the deoxygenation coefficient at base 10 at test temp. is 0.1.

Solution :

The 100% contents of the diluted sample consists of 3% wastewater and 97% of aerated water used for dilution

Hence its D.O = D.O. of waste water × its content + D.O. of dilution water × its content

$$= 0.6\times 0.03 + 3.0\times 0.97 = 0.018 + 2.91$$
$$= 2.928 \text{ mg}/l$$

D.O. of the incubated sample after 5 days = 0.8 mg/*l*

Thus, *D.O.* consumed in oxidising organic matter = 2.928 – 0.8 = 2.128 mg/*l*

∴ B.O.D. of 5 days = D.O. consumed × Dilution factor

$$= 2.128\times\frac{100}{3} = 70.93 \text{ mg}/l$$

Ultimate B.O.D. is given by *L*

using equation, we have, $$Y_t = L\left[1-(10)^{-K_D \cdot t}\right]$$

or $$Y_t = L\left[1-(10)^{-K_D \cdot 5}\right] \quad \text{...(i)}$$

The value of K_D at test temp. is given as 0.1. Substituting the known values in equation (i) above, we have

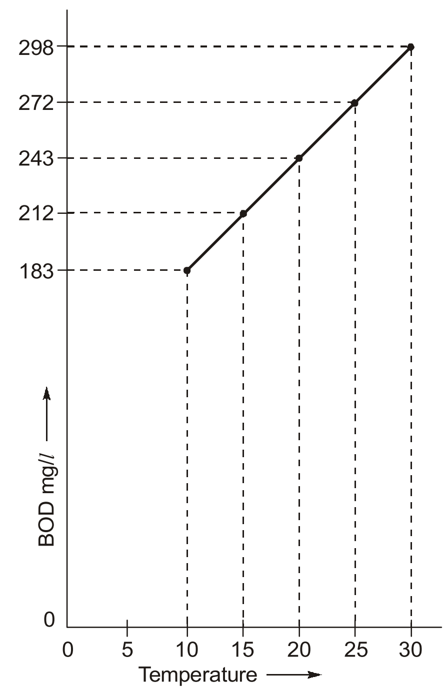
$$70.93 = L\left[1-(10)^{-0.1\times 5}\right] = L\left[1-(10)^{-0.5}\right]$$

$$= L\left[1-\frac{1}{(10)^{0.5}}\right] = L\left[1-\frac{1}{3.16}\right]$$

$$= L[1-0.316] = L \times 0.684$$

or $$L = \frac{70.93}{0.684} = \mathbf{103.7\ mg/}\boldsymbol{l}$$

Q.2 The 3 day 15°C BOD of a sample of sewage is 150 mg/l. Draw a graph of 5 day BOD as a function of temperature in the range 10°C to 30°C in steps of 5°C.



Solution:

Assume: K_D at 20°C = 0.1

Then K_D at 15°C is given as

$$K_{D(T)} = K_{D(20°)}[1.047]^{T-20}$$

or $$K_{D(15)} = 0.1[1.047]^{15-20°}$$

$$= 0.1(1.047)^{-5}$$

$$= \frac{0.1}{(1.047)^5} = 0.079$$

Now, using

$$Y_{t \text{ at } T} = L\left[1-(10)^{-K_D \cdot t}\right], \text{ we have}$$

$$Y_{3 \text{ at } 15} = 150$$

$$= L\left[1-(10)^{-0.079\times 3}\right]$$

$$= L\left[1-\frac{1}{(10)^{0.237}}\right] = 0.422\,L$$

or $$L = 355.53 \text{ mg/}l$$

$$K_{D(10°C)} = 0.1[1.047]^{10-20} = 0.063$$

$$K_{D(15°C)} = 0.1[1.047]^{25-20} = 0.1258$$

$$K_{D(20°C)} = 0.1[1.047]^{30-20} = 0.1583$$

(i) $$Y_{5 \text{ at } 10°C} = 355.33[1-(10)^{-0.063\times 5}] = 183 \text{ mg/}l$$

(ii) $$Y_{5 \text{ at } 15°C} = 355.33[1-(10)^{-0.079\times 5}] = 212 \text{ mg/}l$$

(iii) $$Y_{5 \text{ at } 20°C} = 355.33[1-(10)^{-0.1\times 5}] = 243 \text{ mg/}l$$