

8.3 DISSOLVED OXYGEN (DO) IN WATER AND ITS IMPORTANCE

Oxygen is important to all life. Dissolved oxygen is the form of oxygen in water that is freely available to aquatic plants and animals. Dissolved oxygen is vital to fish and other aquatic life and for the prevention of odors. Oxygen is transferred from the atmosphere into surface waters, as well as being produced by aquatic plants, algae and phytoplankton as a byproduct of photosynthesis. Once dissolved in water, oxygen diffuses throughout a water body very slowly since distribution depends on the movement of aerated water by turbulence and currents, water flow and thermal upwelling. Figure 8.3 depicts a stream flowing with dissolving oxygen and pollutants.



Fig. 8.3 A stream flowing with dissolved oxygen and pollutants

Oxygen in water is measured as dissolved oxygen (DO). One unit of measure of dissolved oxygen in water is parts per million (ppm) which is the number of oxygen (O_2) molecules per million total molecules in a sample. It is also defined as the number of moles of molecular oxygen (O_2) dissolved in a litre of water at a temperature, expressed as mg O_2/l . A high percentage of dissolved oxygen is conducive to supporting aquatic flora and fauna, such as algae, plants, fish, mollusks, and invertebrates. A low percentage or depleted of dissolved oxygen indicates a negative impact on a body of water, which results in an abundance of worms and fly larvae. Aquatic life uses oxygen that is dissolved in the water and is in much smaller quantities than in the air. If more oxygen is consumed than is produced, dissolved oxygen levels decline and some sensitive animals may move away, weaken, or die. Figure 8.4 gives a graphical depiction of dissolved oxygen and aquatic life in water.

One of the best indicators of the health of a body of water, such as a river, stream, lake, or pond, ecosystem is the dissolved oxygen (DO) parameter. Dissolved oxygen can range from 0–18 mg O_2/l . Most natural water systems require 5–6 mg O_2/l to support a diverse population. Oxygen enters the water either by direct absorption from the atmosphere or by plant photosynthesis. The oxygen is used by plants and animals for respiration and by the aerobic bacteria which consume oxygen during the process of decomposition. When organic matter such as animal waste or improperly treated wastewater enters a body of water, algae growth increases when organic matter such as animal waste or improperly treated waste water enters a body of water causing the dissolved oxygen levels to decrease as the plant material dies off and is decomposed through the action of the aerobic bacteria.

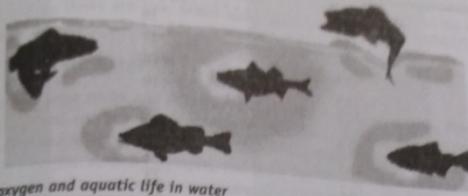
Fig. 8.4

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Fig. 8.4

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Q.3.4 Dissolved oxygen and aquatic life in water

Q.3.1 Factors Affecting Dissolved Oxygen Levels

1. Water temperature—when temperature decreases, more oxygen dissolves in water; when temperature increases, dissolved oxygen decreases
2. Aquatic plant populations
3. Stream flow
4. Altitude/atmospheric pressure
5. Human activities
6. Water discharge—when water discharge (flow) increases, dissolved oxygen increases
7. Organic waste (such as leaves, sewage, industrial waste, agricultural/fertiliser runoff, and fecal matter) build up—when it increases, dissolved oxygen decreases.



Q.3.5 A completely polluted lake

Temperature is important for the ability of oxygen to dissolve and has different solubility's at different temperatures.

°C	mg/l	°C	mg/l
0	14.6	16	10.0
1	14.2	17	9.8
2	13.8	18	9.6
3	13.5	19	9.4
4	13.1	20	9.2
5	12.8	21	9.0
6	12.5	22	8.9
7	12.2	23	8.7
8	11.9	24	8.6
9	11.6	25	8.4
10	11.3	26	8.2
11	11.1	27	8.1
12	10.9	28	7.9
13	10.6	29	7.8
14	10.4	30	7.7
15	10.2	31	7.4

Weather, temperature and salinity affect amounts of dissolved oxygen (DO). Cold, fresh water holds more oxygen than warm or salty water. If DO levels are severely low, large quantities of fish may die.



Fig. 8.6 Fishes die due to low level DO in water

Low DO is also caused by fertiliser and manure runoff from streets, lawns and farms. Fertilisers and faecal matter encourage the growth of too much algae, which uses up the oxygen quickly. Plants and animals die and are decayed by bacteria, which also uses up a great deal of oxygen.

The stream system gains oxygen from the atmosphere and from aquatic plants as a result of photosynthesis. Running water, because of its churning, dissolves more oxygen than still water. Respiration by aquatic animals, decomposition, and various other chemical reactions consume oxygen. DO levels fluctuate seasonally and over a 24-hour period. They vary with water temperature and altitude. Cold water holds more oxygen than warm water (see table) and water holds less oxygen at higher altitudes. Thermal discharges, such as waste

used to cool machinery in a manufacturing plant or a power plant, raise the temperature of water and lower its oxygen content. Aquatic animals are most vulnerable to lowered DO levels in the early morning on hot summer days when stream flows are low, water temperatures are high, and aquatic plants have not been producing oxygen since sunset.

8.3.2 Sources of DO in Water

Interaction as water moves over rocks and debris. Aeration from wind and waves. Photosynthesis of aquatic plants. When the dissolved oxygen levels decreases it effects the number and types of aquatic macro invertebrates which live in a water ecosystem. Species which cannot tolerate decreases in dissolved oxygen levels include mayfly nymphs, stonefly nymphs, caddisfly larvae and beetle larvae. As the dissolved oxygen levels decrease, these pollution-intolerant organisms are replaced by the pollution-tolerant worms and fly larvae.

Dissolved oxygen concentrations arise from the interaction between:

- oxygen produced by photosynthesis
- oxygen consumed by aerobic respiration, nitrification and chemical oxidation within the water environment; and
- the exchange of oxygen with the atmosphere.

Natural processes (e.g. weather, tides and currents) and human pollution (particularly organic matter) can result in severe reductions in dissolved oxygen levels. Both anoxia (no oxygen) and hypoxia (very low oxygen) are harmful to most marine animals causing:

- animal kill
- a decrease in the available habitat and limiting animal movements.

Low dissolved oxygen levels can also result in reduction conditions within the sediments which may cause previously bound nutrients and toxicants to be released into the water column. Observed decreases in dissolved oxygen of individual water bodies are mainly related to increased organic matter load (e.g. from sewage treatment plants and industry, organic runoff or algal blooms) which leads to increased bacterial activity (decomposition by aerobic microorganisms). This increase in activity results in increased oxygen consumption and can deplete available oxygen. Low oxygen levels generally affect bottom waters first and most severely.

Dissolved oxygen levels change and vary according to the time of day, the weather and the temperature. Large fluctuations in dissolved oxygen levels over a short period of time may be the result of an algal bloom. While the algae population is growing at a fast rate, dissolved oxygen levels increase. Soon the algae begin to die and are decomposed by aerobic bacteria, which use up the oxygen. As a greater number of algae die, the oxygen requirement of the aerobic decomposers increases, resulting in a sharp drop in dissolved oxygen levels. Following an algal bloom, oxygen levels can be so low that fish and other aquatic organisms suffocate and die.

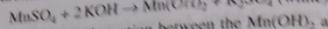
8.3.3 Theory of Winkler's Method for DO Determination

The Winkler method (1888), otherwise known as the iodometric technique, is the most precise and reliable titrimetric procedure for DO analysis. The chemistry of this test is based on the addition of a manganese solution followed up by a strong alkali solution. The DO present rapidly forms hydroxide salts with the manganese. The colour of the precipitate formed is an initial indicator of how much DO is present. In the presence of iodide ions in an acidic solution, the oxidised manganese reverts back to the divalent state and

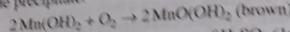
the liberated iodine is equivalent to the original DO content. This iodine is then titrated with a standard thiosulfate solution.

The redox chemistry of Winkler's method is as follows:

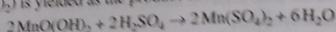
Manganous sulfate reacts with the potassium hydroxide-potassium iodide to produce a white flocculent precipitate of manganous hydroxide:



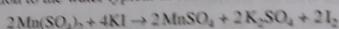
If there is any DO in the water a second reaction between the Mn(OH)_2 and DO occurs immediately, form a brownish manganic oxide precipitate.



When the samples are ready to be titrated, requisite amount of H_2SO_4 (1:1 sulphuric acid) is added to each sample and the bottles are inverted several times in order to completely redissolve the brownish precipitate. Manganic sulphate ($\text{Mn}(\text{SO}_4)_2$) is yielded as the product of this reaction:



The $\text{Mn}(\text{SO}_4)_2$ immediately reacts with the potassium iodide (KI) added, liberating the number of moles of iodine exactly equivalent to the number of moles of oxygen present in the sample. The release of iodine (I_2) imparts a brown colouration to the water typical of iodine.



Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) then reacts with the released I_2 to give an accurate estimate of the DO in the original sample. The sample is then titrated to a pale, straw colour before the starch indicator is added. This will change the solution blue. The titration end point is when the blue colour disappears.

Sources of Error As mentioned earlier, the sources of error listed below are only found infrequently in water settings.

1. If nitrates are present in large quantities, high values for oxygen may be obtained because of the following chemical reaction:



2. If hydrogen sulfide is present, the Winkler method for determining oxygen is not applicable. Hydrogen sulfide will react with the dissolved oxygen and with iodine.

For example, one possible reaction is:



The sulphur formed is almost colloidal in nature and such waters will be devoid of oxygen, except for the possibility of an interface zone where $\text{O}_2 + \text{H}_2\text{S}$ may be present. The hydrogen sulphide reacts with iodine and, if present in sufficient quantities, may be determined iodometrically.

Calculation of DO

$$1 \text{ mole of O}_2 = 2 \text{ moles of I}_2 = 4 \text{ moles of Na}_2\text{S}_2\text{O}_3$$

$$1 \text{ mol of Na}_2\text{S}_2\text{O}_3 \equiv 1/4^{\text{th}} \text{ mole of O}_2 \equiv 8 \text{ g of O}_2$$

$$1 \text{ ml of } 1 \text{ N Na}_2\text{S}_2\text{O}_3 \equiv 8 \text{ mg O}_2$$

$$'V' \text{ ml of } 0.005 \text{ N Na}_2\text{S}_2\text{O}_3 \equiv 8 \times V \times 0.005 \text{ N}$$

Therefore,

$$\text{DO of water sample} \equiv \frac{8 \times \text{Vol} \times 0.05 \times 1000}{25} \text{ at } t^\circ\text{C}$$

8.4 BIOLOGICAL OXIDATION

8.4.1 Introduction

The BOD is the amount of oxygen consumed by the microorganisms in a water sample over a period of time.

When organic material and food waste is added to water, microorganisms decompose it.

BOD depletion in water is same as DO depletion.

Sources of organic matter include pulp and paper systems; animal wastes; biological wastes; aerobic decomposition of organic matter.

Nitrate formation is due to the decomposition of plant nutrients.

When organic matter is added to water, it contributes to the DO depletion. A DO depletion also increases the bottom water temperature which is high and results in a DO depletion.

8.4.2 Biological Oxygen Demand

The DO depletion is due to the oxidation of organic matter by the microorganisms. It is used to determine the efficiency of the treatment process.

A DO depletion must be avoided by the treatment process.

8.4 BIOLOGICAL OXYGEN DEMAND (BOD)

8.4.1 Introduction to BOD

The BOD is an important measure of water quality. It is a measure of the amount of oxygen needed (in milligrams per liter or ppm) by bacteria and other microorganisms to oxidize the organic matter present in a water sample over a period of 5 days. The BOD of drinking water should be less than 1. That of raw sewage may run to several hundred. It is also called the "biological" oxygen demand.

When organic matter decomposes, microorganisms (such as bacteria and fungi) feed upon this decaying material and eventually it becomes oxidized. Microorganisms such as bacteria are responsible for decomposing organic waste. When organic matter such as dead plants, leaves, grass clippings, manure, sewage, or even food waste is present in a water supply, the bacteria will begin the process of breaking down this waste. When this happens, much of the available dissolved oxygen is consumed by aerobic bacteria, robbing other aquatic organisms of the oxygen they need to live.

BOD directly affects the amount of dissolved oxygen in rivers and streams. The more rapidly oxygen is depleted in the stream, the greater the BOD. This means less oxygen is available. The detriment of high BOD is same as low dissolved oxygen; aquatic organisms become stressed, suffocate and die.

Sources of BOD include leaves and woody debris; dead plants and animals; animal manure; effluents from pulp and paper mills; wastewater treatment plants, feedlots, and food-processing plants; failing septic systems; and urban storm water runoff.

Biological oxygen demand (BOD) of a sewage is defined as the number of milligrams of dissolved oxygen required for the oxidation of biologically oxidisable impurities present in 1000 ml of waste water under aerobic conditions at 20°C over a period of 5 days.

Nitrates and phosphates in a body of water can contribute to high BOD levels. Nitrates and phosphates are plant nutrients and can cause plant life and algae to grow quickly.

When plants grow quickly, they also die quickly. This contributes to the organic waste in the water, which is then decomposed by bacteria. This results in a high BOD level. The *temperature* of the water can also contribute to high BOD levels. For example, warmer water usually will have a higher BOD level than colder water. As water temperature increases, the rate of photosynthesis by algae and other plant life in the water also increases. When this happens, plants grow faster and also die faster. When plants die, they fall to the bottom where they are decomposed by bacteria. The bacteria require oxygen for this process so the BOD is high at this location. Therefore, increased water temperatures will speed up bacterial decomposition and result in higher BOD levels.

8.4.2 Determination of BOD

The five-day Biochemical Oxygen Demand (BOD₅) assay is a standardised assessment of the amount of oxidizable, or respirable, organic matter in water. It is the amount of oxygen (in mg/l) required by bacteria to oxidize the organic molecules aerobically. Oxygen consumed by inorganic compounds is also measured by this test, which is why it is referred to as biochemical oxygen rather than just biological oxygen demand. It is used as an index of the amount of organic pollution of the water and is routinely employed to measure the efficiency of wastewater treatment plants in removing organic matter from wastewater or in assessing the effect of effluents on the trophic status of natural waters.

Any wastes, such as municipal sewage, abattoir discharge, and some industrial wastes with high BOD, must be treated to remove or lower the BOD before release into the receiving water. This removal of BOD by the wastewater treatment plant is inevitably biological but may be either aerobic or anaerobic.

1. Overview A sample of the water of interest is placed in a BOD bottle and its dissolved oxygen concentration measured. The bottle is sealed and incubated in the dark for 5 days at 20°C. At the end of the incubation time the DO is measured again. The drop in DO over the incubation period is due to the oxygen used by bacteria to oxidise the organic material in the sample. BOD is high in organically polluted waters and low in pristine water. It is very high in wastewater, some industrial effluents, and sludge/wastes.

2. Dilution Waters with high concentrations of organic material will not contain sufficient dissolved oxygen for complete oxidation. In this case an undiluted sample will become anaerobic sometime during the five-day incubation period and no useful information will be gained from the procedure. It is necessary to dilute such samples so that there will be sufficient oxygen present to oxidise all the organic matter, with a little oxygen left over. The amount of dilution required by any given sample must be determined by trial and error or past experience. It is customary to prepare multiple dilutions, usually three, of each sample to assist in finding one that is usable.

Although the best dilutions to use must be determined by trial and error, the following guidelines can be used to approximate the correct dilution.

Sample	Dilution %
Strong industrial wastes	<1
Raw and settled wastewater	1-5
Biologically treated effluent	5-25
Polluted receiving waters	25-100

3. Dilution Water Bacterial growth requires inorganic nutrients as well as organic compounds and these must be added to the dilution water to ensure their presence. The dilution water is also buffered to ensure a pH suitable for bacterial growth.

4. Seeding After dilution, the sample must be seeded with a bacterial source to ensure the presence of bacteria capable of degrading the organic material in the sample. Non-chlorinated treatment plant secondary effluent or raw sewage may be used for this but it is preferable to use a commercial preparations of lyophilised bacteria such as Polyseed®.

5. Calculation Calculate the five-day BOD using the simplified expression

$$\text{BOD} = (D_1 - D_2)/P$$

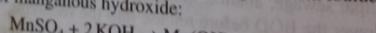
where D_1 = initial DO, D_2 = final DO, and P = decimal volumetric fraction of sample used, e.g. a 75 ml sample diluted to 300 ml would be a 25% solution and $P = 0.25$.

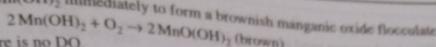
8.4.3 BOD by Winkler's Method

Principle Winkler's method is based on the fact that in alkaline medium, DO oxidises Mn^{2+} to Mn^{4+} , which in acidic medium oxidises I^- to free iodine. The amount of iodine released which can be titrated with a standard solution of sodium thiosulphate, is thus equivalent to the DO originally present.

The following reactions take place:

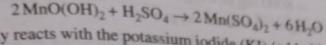
Manganous sulphate reacts with the potassium hydroxide-potassium iodide (alkaline-iodide) to produce a white flocculent precipitate of manganous hydroxide:



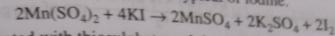


If the precipitate is white there is no DO.

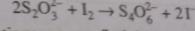
Manganic oxide reacts with added H_2SO_4 to give manganic sulphate ($Mn(SO_4)_2$) as the product of this reaction:



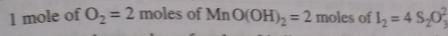
The $Mn(SO_4)_2$ immediately reacts with the potassium iodide (KI) (added initially as part of alkali-iodide), liberating the iodine exactly equivalent to the number of moles of oxygen present in the sample. The release of iodine (I_2) imparts a brown coloration to the water typical of iodine.



The liberated iodine is titrated with thiosulphate and the reaction is:



From the above stoichiometric equations, we can find that:



Therefore, after determining the number of moles of iodine produced we can determine the number of moles of oxygen molecules present in the water sample. Dissolved oxygen concentrations are generally expressed in $mg\ O_2/L$.

From the titre values BOD is calculated.

Procedure A known volume of the sewage water is diluted to a known volume with fresh water. Equal quantities of the diluted water are taken in two BOD bottles. In the first bottle BOD is determined immediately as follows. To a known volume of diluted water 5 ml of $MnSO_4$ solution and 5 ml of alkaline KI are added and shaken for about 15 minutes till MnO_2H_2O gets precipitated. Then the precipitate is dissolved in 2 ml of H_2SO_4 and the liberated I_2 is titrated against standard sodium thiosulphate. The titre value is called blank value and it indicates the total dissolved oxygen available at the start of the experiment.

The water in the second bottle is incubated under aerobic conditions for 5 days and BOD is determined as described above. The litre value indicates dissolved oxygen present after 5 days.

- When dilution water is not needed:

$$BOD_5, \text{ mg/l} = \frac{D_1 - D_2}{P}$$

where D_1 = DO of diluted sample immediately after preparation, mg/l,

D_2 = DO of diluted sample after 5 d incubation at $20^\circ C$, mg/l, and

P = decimal volumetric fraction of sample used.

Alternatively,

- Calculation:

Volume of sewage water taken = V_1 ml

Volume of water after dilution = V ml

Volume of diluted water taken for titration = V_2 ml

Volume of this required for blank = A ml

Volume of thiosulphate required after 5 days = B ml

Dissolved oxygen available at the beginning = A ml of $Na_2S_2O_3$

Dissolved oxygen available after 5 days = B ml of $\text{Na}_2\text{S}_2\text{O}_3$ solution.

Dissolved oxygen used up for biological oxidation in 5 days = $(A - B)$ ml of $\text{Na}_2\text{S}_2\text{O}_3$

Normality of $\text{Na}_2\text{S}_2\text{O}_3 = N$

1000 ml of 1 N $\text{Na}_2\text{S}_2\text{O}_3 = 8$ g of oxygen

= 8000 mg of oxygen

1 ml of 1 N $\text{Na}_2\text{S}_2\text{O}_3 = 8$ mg of dissolved oxygen

$(A - B)$ ml $\times N \text{ Na}_2\text{S}_2\text{O}_3 = (A - B) \times N \times 8 \text{ mg oxygen}$

V_2 ml of diluted waste water requires $(A - B) \times N \times 8 \text{ mg of oxygen}$

$$V \text{ ml of diluted waste water requires} = \frac{(A - B) \times N \times 8 \times V}{V_2} \text{ mg of oxygen}$$

$$\text{BOD of } v_1 \text{ ml of waste water} = \frac{(A - B) \times N \times 8 \times V}{V_2}$$

$$\therefore \text{BOD of 1000 ml of waste water} = \frac{(A - B) \times N \times 8 \times v_2}{V} \times \frac{1000}{v_1} \text{ mg of oxygen/l.}$$

where, A = Blank titre value B = titre value after 5 days, v_1 is the volume of waste water taken, v_2 is the volume after dilution and V is the volume taken for titration.

Example 11 • 25 ml of waste was diluted to 500 ml and equal volumes are filled in two BOD bottles.

In the blank titration 100 ml of diluted waste water when titrated immediately required 6.1 ml of 0.02 N $\text{Na}_2\text{S}_2\text{O}_3$. 100 ml of the incubated sample after 5 days required 3.6 ml of same $\text{Na}_2\text{S}_2\text{O}_3$. Calculate BOD of the wastewater.

Solution

Method I:

Volume of waste water = 25 ml

Volume of after dilution = 500 ml

Volume of dilute water used for titration = 100 ml

Blank titre value = 6.1 ml .02 N $\text{Na}_2\text{S}_2\text{O}_3$

Titre value after 5 days = 3.6 ml .02 N $\text{Na}_2\text{S}_2\text{O}_3$

Dissolved oxygen at the beginning of the experiment is equivalent to 6.1 ml 0.02 N $\text{Na}_2\text{S}_2\text{O}_3$.

Dissolved oxygen after 5 days is equivalent to 3.6 ml 0.02 N $\text{Na}_2\text{S}_2\text{O}_3$

Dissolved oxygen used up by wastewater in 5 days is = $(6.1 - 3.6)$

$$= 2.5 \text{ ml .02 N } \text{Na}_2\text{S}_2\text{O}_3$$

1 ml 1 N $\text{Na}_2\text{S}_2\text{O}_3 = 8$ mg oxygen

2.5 ml .02 N $\text{Na}_2\text{S}_2\text{O}_3 = 2.5 \times 0.02 \times 8 = 0.4$ mg oxygen

100 ml of diluted water = 0.4 mg oxygen

25 ml of original waste water = 500 ml dilute waste water

$$= \frac{0.4 \times 500}{600}$$

$$= 2 \text{ mg oxygen}$$

1000 ml of orig

BOD of waste

Method II:

BOD of 1000

Given

$A = 6.1 \text{ ml.}$

$V = 100 \text{ ml.}$

Example 12

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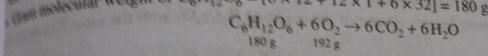
$$\text{mg/l of original waste water} = \frac{2 \times 1000}{25} \\ = 80 \text{ mg oxygen}$$

(A - B) $\times N \times 8 \times v_2$
 $\text{mg/l of 1000 ml of waste water} = \frac{(A - B) \times N \times 8 \times v_2}{V} \times \frac{1000}{v_1} \text{ mg of oxygen/l}$

Given
 $v_1 = 6.1 \text{ ml}$, $B = 3.6 \text{ ml}$, $v_1 = 25 \text{ ml}$ of waste water taken; $V_2 = 500 \text{ ml}$, the volume after dilution and
 $V = 100 \text{ ml}$, the volume taken for titration and $N = 0.02 \text{ N}$

$$= \frac{[6.1 - 3.6] \times 0.02 \times 8 \times 500 \times 1000}{100 \times 25} = 80 \text{ mg/l}$$

Example 12 Calculate the BOD value of a sewage sample containing 9.2 mg/l of organic matter with the formula $C_6H_{12}O_6$.

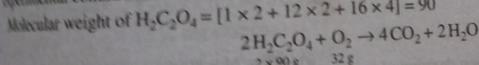


Therefore,
 180 mg/l of $C_6H_{12}O_6$ needs 192 mg/l of oxygen for complete oxidation under experimental conditions in sewage water.

If sewage water contains 9.2 mg/l , then it needs $\frac{9.2 \times 192}{180} \text{ mg/l}$ of oxygen to oxidise

Hence, BOD of the sewage water = 9.813 mg/l .

Example 13 An effluent water sample emerging out from a chemical factory is found to contain only a organic compound of molecular formula $H_2C_2O_4$. If the waste water sample contain 60 mg/litre of the above compound, what would be the amount of oxygen required to oxidise by micro organisms under experimental conditions of BOD estimation. [$C = 12$, $H = 1$ and $O = 16$].



Therefore,
 180 mg/litre of $H_2C_2O_4$ in waste water requires 32 mg of oxygen to oxidise into carbon dioxide and water.

In a BOD experiment, if waste water contains 150 mg/l of $H_2C_2O_4$, then the amount of oxygen needed to oxidise the organic impurity = $\frac{60 \times 32}{180} = 10.67 \text{ mg/l}$.

8.5 CHEMICAL OXYGEN DEMAND

In environmental chemistry, the *chemical oxygen demand* (COD) test is commonly used to indirectly measure the amount of organic compound in water. Most applications of COD determine the amount of organic

pollutants found in surface water (e.g. lakes and rivers), making COD a useful measure of water quality. It is expressed in milligrams per liter (mg/l), which indicates the mass of oxygen consumed per liter of solution. Older references may express the units as parts per million (ppm).

COD of a waste water is the number of milligrams of oxygen required to oxidise the impurities present in 1000 ml of waste water using strong oxidising agents like acidified $K_2Cr_2O_7$.

COD represents the total amount of oxygen required to oxidise all oxidisable impurities in a sample of sewage wastes. COD is always greater than BOD since in COD measurement both biodegradable and non-biodegradable load are completely oxidised. The difference in COD and BOD is equivalent to the quantity of biologically resistant organic matter.

8.5.1 Determination of COD

Principle A known volume of the wastewater sample is refluxed with a known excess of $K_2Cr_2O_7$ solution in H_2SO_4 medium containing $HgSO_4$ (catalyst) and Ag_2SO_4 [which retains halides] for about 1 1/2 hr for the oxidation to be complete. A part of the $K_2Cr_2O_7$ is used up for the oxidation of impurities. The remaining $K_2Cr_2O_7$ is determined by titration with standard FAS solution using ferroin as indicator. The endpoint is the change of colour from blue green to reddish brown.

A blank is performed by titrating known volume of the acidified $K_2Cr_2O_7$ with the same FAS using the same indicator.

$$\text{COD of water sample} = \frac{(A - B) \times M \times 8000 \text{ ml}}{\text{Volume of sample}} \text{ mg/l}$$

where A = Blank titre value of $K_2Cr_2O_7$ vs FAS and

B = Volume of FAS consumed for unreacted $K_2Cr_2O_7$ of the solution.

M = Molarity of FAS solution.

Procedure 25 ml of waste water is pipetted out into a round bottomed flask. 10 ml of $K_2Cr_2O_7$ is pipetted out into the same flask along with one test tube full of 1:1 H_2SO_4 containing $HgSO_4$ and Ag_2SO_4 . The flask is filled with a reflux water condenser and the mixture is refluxed for 2 hours. The contents are cooled and transferred to a conical flask. 5 drops of ferroin indicator is added to it and titrated against FAS taken in the burette till the colour changes from blue green to red brown. Same volume of $K_2Cr_2O_7$ is pipetted out, mixed with sulphuric acid and ferroin and titrated against same FAS to get blank titre value.

Calculation:

Method I

$$\text{Chemical oxygen demand of water} = \frac{(A - B) \times M \times 8000}{V} \text{ mg/l}$$

where A = FAS (ml) used for blank

B = FAS (ml) used for sample

M = Molarity of FAS

V = Volume of sample (ml).

Method II

Volume of waste water = V ml

Solution of standard FAS used in sample titration = B ml

Volume of standard FAS in blank titration = A ml

FAS equivalent
Normality of
 V ml of wa
1000 ml 1
1 ml 1 M F
 $\therefore (A - B)$
 V ml of wa
1000 ml o
where, V
the molar

Example 1
 $K_2Cr_2O_7$ a
of same O

Solution
Method I

Method

25 ml

25 K_2

25 ml

1 ml

8.2 n

25 n

100

\therefore

Examp

K_2C

Solu

Met

FAS equivalent of $K_2Cr_2O_7$ consumed by V ml waste water = $(A - B)$ ml

Normality of FAS (N) = Molarity of FAS (M)

1 ml of waste water = used up $K_2Cr_2O_7$ = $(Y - X)$ ml N normal FAS

1000 ml 1 M FAS = 8 g of oxygen = 8000 mg oxygen

1 ml 1 M FAS = 8 mg of oxygen

$\therefore (A - B)$ ml Normal FAS = $(A - B) \times M \times 8$ mg oxygen

1 ml of waste water requires $(A - B) \times M \times 8$ mg oxygen

1000 ml of water (COD) requires $(A - B) \times M \times 8000/V$ mg/l

where, V is the volume of waste, A is the blank titre value B is the titre value with the sample, and M is the molarity of FAS.

Example 14 25 ml of wastewater was mixed with 25 ml of $K_2Cr_2O_7$, acidified and refluxed. The unreacted $K_2Cr_2O_7$ acidified required 8.2 ml of FAS. In a blank titration 25 ml of $K_2Cr_2O_7$ acidified required 16.4 ml of same 0.2 N FAS. Calculate COD of wastewater.

Solution

Method I

$$\text{COD of wastewater} = \frac{(A - B) \times M \times 8000}{V} \text{ mg/l}$$

$$= \frac{[16.4 - 8.2] \times 0.2 \times 8000}{25}$$

$$= 524.8 \text{ mg/l}$$

Method II

25 ml waste + 25 ml $K_2Cr_2O_7$ = 8.2 ml 0.2 N FAS

25 $K_2Cr_2O_7$ alone = 16.4 ml 0.2 FAS

25 ml of waste water = used up $K_2Cr_2O_7$ = $(18.2 - 16.4)$ ml 0.2 N FAS

= 8.2 ml 0.2 FAS

1 ml 1 N FAS = 8 mg of oxygen

8.2 ml 0.2 N FAS = $8 \times 8.2 \times 0.2$ mg oxygen

= 13.12 mg oxygen

25 ml of waste water requires 13.12 mg oxygen

$$1000 \text{ ml of waste water requires } \frac{13.12 \times 1000}{25} = 524.8 \text{ mg oxygen}$$

\therefore COD of the waste water = 524.8 mg oxygen.

Example 15 Calculate COD of effluent sample when 25 cm³ of the effluent required 8.3 cm³ 0.001 M $K_2Cr_2O_7$ for oxidation [given molar mass of $K_2Cr_2O_7$ = 294].

Solution

Method I

$$\text{COD of wastewater} = \frac{(A - B) \times M \times 8000}{V} \text{ mg/l}$$

quality. It is
of solution,
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sample of
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quantity of

γ solution
hr for the
remaining
point is the

using the

sipetted
the flask
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in the
mixed

FAS equivalent of $K_2Cr_2O_7$ consumed by V ml waste water = $(A - B)$ ml

Normality of FAS (N) = Molarity of FAS (M)

V ml of waster water = used up $K_2Cr_2O_7$ = $(Y - X)$ ml N normal FAS

1000 ml 1 M FAS = 8 g of oxygen = 8000 mg oxygen

1 ml 1 M FAS = 8 mg of oxygen

$\therefore (A - B)$ ml Normal FAS = $(A - B) \times M \times 8$ mg oxygen

V ml of waste water requires $(A - B) \times M \times 8$ mg oxygen

1000 ml of water (COD) requires $(A - B) \times M \times 8000/V$ mg/l

where, V is the volume of waste, A is the blank titre value B is the titre value with the sample, and M is the molarity of FAS.

Example 14 25 ml of wastewater was mixed with 25 ml of $K_2Cr_2O_7$, acidified and refluxed. The unreacted $K_2Cr_2O_7$ acidified required 8.2 ml of FAS. In a blank titration 25 ml of $K_2Cr_2O_7$, acidified required 16.4 ml of same 0.2 N FAS. Calculate COD of wastewater.

Solution

Method I

$$\text{COD of wastewater} = \frac{(A - B) \times M \times 8000}{V} \text{ mg/l}$$

$$= \frac{[18.4 - 16.4] \times 0.2 \times 8000}{25}$$

$$= 524.8 \text{ mg/l}$$

Method II

$$25 \text{ ml waste} + 25 \text{ ml } K_2Cr_2O_7 = 8.2 \text{ ml } 0.2 \text{ N FAS}$$

$$25 \text{ } K_2Cr_2O_7 \text{ alone} = 16.4 \text{ ml } 0.2 \text{ FAS}$$

$$25 \text{ ml of waste water} = \text{used up } K_2Cr_2O_7 = (18.2 - 16.4) \text{ ml } 0.2 \text{ N FAS}$$

$$= 8.2 \text{ ml } 0.2 \text{ FAS}$$

$$1 \text{ ml } 1 \text{ N FAS} = 8 \text{ mg of oxygen}$$

$$8.2 \text{ ml } 0.2 \text{ N FAS} = 8 \times 8.2 \times 0.2 \text{ mg oxygen}$$

$$= 13.12 \text{ mg oxygen}$$

$$25 \text{ ml of waste water requires } 13.12 \text{ mg oxygen}$$

$$1000 \text{ ml of waste water requires } \frac{13.12 \times 1000}{25} = 524.8 \text{ mg oxygen}$$

$$\therefore \text{COD of the waste water} = 524.8 \text{ mg oxygen.}$$

Example 15 Calculate COD of effluent sample when 25 cm^3 of the effluent required 8.3 cm^3 0.001 M $K_2Cr_2O_7$ for oxidation [given molar mass of $K_2Cr_2O_7$ = 294].

Solution

Method I

$$\text{COD of wastewater} = \frac{(A - B) \times M \times 8000}{V} \text{ mg/l}$$

$$6 \text{ N } \text{K}_2\text{Cr}_2\text{O}_7 = 1 \text{ M } \text{K}_2\text{Cr}_2\text{O}_7$$

$$\text{COD of waste water} = (8.3) \times 6 \times 0.001 \text{ N} \times 8000/25 \text{ mg/l}$$

$$= 15.976 \text{ mg/l}$$

Method II

$$1000 \text{ l ml } 1 \text{ N } \text{K}_2\text{Cr}_2\text{O}_7 = 8 \text{ g of oxygen}$$

$$1 \text{ ml } 1 \text{ N } \text{K}_2\text{Cr}_2\text{O}_7 = 8 \text{ mg oxygen}$$

$$\text{Molar mass of } \text{K}_2\text{Cr}_2\text{O}_7 = 294 \text{ and equation mass} = 49$$

$$1 \text{ mole} = 6 \text{ equivalence } 1 \text{ M} = 6 \text{ N}$$

$$1 \text{ ml } 1 \text{ mol} = 6 \text{ ml } 1 \text{ N } \text{K}_2\text{Cr}_2\text{O}_7$$

$$\therefore 1 \text{ ml } 1 \text{ molar } (6 \text{ N}) \text{ K}_2\text{Cr}_2\text{O}_7 = 6 \times 8 = 48 \text{ mg oxygen}$$

$$25 \text{ cm}^3 \text{ wastewater} = 8.3 \text{ cm}^3 \times 0.001 \text{ M } \text{K}_2\text{Cr}_2\text{O}_7$$

$$= 48 \times 8.3 \times 0.001 \text{ mg oxygen}$$

$$25 \text{ cm}^3 \text{ wastewater} = 0.3994 \text{ mg oxygen}$$

$$\therefore 1000 \text{ cm}^3 \text{ wastewater} = 0.03994/25 \times 1000$$

$$= 15.976 \text{ mg oxygen}$$

$$\text{COD of the sample} = 15.976 \text{ mg oxygen.}$$

8.6 SEWAGE & ITS CHARACTERISTICS

Sewage is the liquid waste from toilets, baths, kitchens, etc. that is disposed off via sewers. In many areas sewage also includes some liquid waste from industry and commerce. Any fresh sewage is usually green or yellowish green. With aging, it becomes dark brown. Fresh sewage is odourless but when it becomes stale it produces an abnoxious smell due to the release of gases like H_2S , phosphine, etc. Sewage water is normally turbid and has a temperature slightly higher than ordinary water. It contains dissolved and suspended impurities and also colloidal dispersion. Sewage contains both organic and inorganic impurities. The pH of fresh sewage is higher than 7 (alkaline) but after a few days it becomes less than 7 (acidic). Sewage also contains pathogenic (disease producing) bacteria and non-pathogenic bacteria. There are two types of non-pathogenic bacteria.

Much sewage also includes some surface water from roofs or hard-standing areas. Municipal waste water therefore includes residential, commercial, and industrial liquid waste discharges, and may include storm water runoff.

- (i) *Aerobic bacteria*, live and grow on free oxygen and dissolved oxygen. These bacteria act as catalysts for the oxidation of fresh sewage. The products of oxidation are nitrites, nitrates, sulphates, etc. These do not produce any offensive smell
- (ii) *Anaerobic bacteria*, live and grow in the absence of free oxygen. When the dissolved oxygen content in water decreases below a particular level anaerobic bacteria try to decompose the organic compounds in water and produces methane, H_2S , phosphine etc. responsible for the offensive smell. The water is said to be stale and the process of oxidation is anaerobic oxidation.

8.7 SEWAGE TREATMENT

In essence, sewage treatment has two functions:

- to kill pathogenic bacteria etc.
 - to eliminate oxygen
 - Domestic sewage involves several processes.
 - It causes pollution.
 - Pathogenic bacteria etc.
- Domestic sewage involves three types of processes:
1. primary
 2. secondary
 3. tertiary

- to kill pathogens (whatever they are).
 - to eliminate harmful chemicals from the water.
 - chemicals that are toxic and the bulk of organic chemicals that cause the depletion of life-supporting oxygen in the receiving waters of a stream, river or lake.
 - Domestic sewage contains colour, bad odour, organic and inorganic impurities, pathogenic bacteria etc. If this sewage is discharged into rivers, lakes and sea, the water in them get polluted and causes several harmful effects.
 - It colours and produces bad odour affecting quality of water.
 - It causes reduction in dissolved oxygen. This endangers the life of fish and aquatic life.
 - Pathogenic bacteria lead to water borne diseases.
- Domestic sewage therefore needs proper treatment before it is run into natural water bodies. Treatment of sewage involves removal of organic impurities, suspended and floating materials, inorganic salts, pathogenic bacteria etc.

Sewage treatment is carried out in three stages:

1. primary treatment
2. secondary treatment, and
3. tertiary treatment, as depicted in Fig. 8.7.

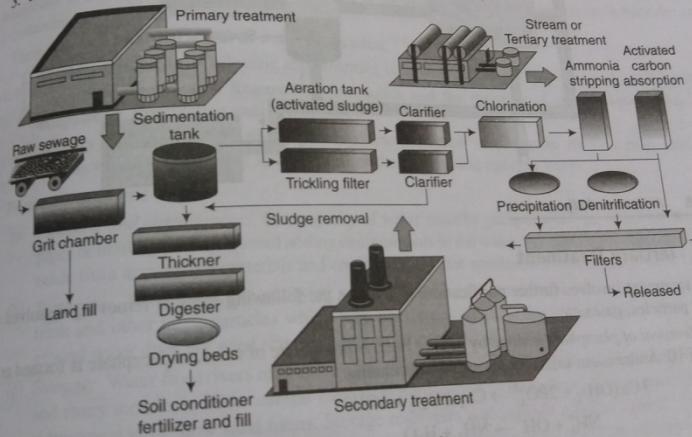


Fig. 8.7 Schematic flow diagram indicating sewage treatment

8.7.1 Primary Treatment

Primary treatment is used to remove *suspended and floating solids* from waste water by physical and chemical methods. It involves the following steps:

- (i) Screening using bar screens and mesh screens floating, suspended and coarse particles are removed by passing sewage water through it.

- (ii) *Slit and grit removal:* Sand, powdered glass, etc. called grit, are removed by slowly passing sewage water through grit chambers. Heavier sand and broken glass settle down by gravity.
- (iii) *Removal of oil and grease:* Sewage water is kept in a skimming tank and compressed air is passed through it. Oil and grease form froth and float on the surface. It is skimmed off.
- (iv) *Sedimentation process:* In this process fine suspended particles which do not settle down by gravity are coagulated by the addition of coagulating agents like alum, FeSO_4 etc. The sedimented particles are filtered off.

8.7.2 Secondary Treatment (Biological Treatment)

Activated Sludge Method Wastewater after sedimentation is mixed with required quantity of activated sludge (containing micro organisms and aerobic bacteria) in an aeration tank as shown in Fig. 8.8. The mixture is aerated by blowing air through it for several hours. Because of the aerobic conditions the organic matter in the sewage is fully oxidised. The purified water plus sludge is sent to a tank where sludge settles down. A part of the sludge is used for purification of fresh batch of sewage while the rest is pumped to sludge disposal tank. Purified water is pumped out and collected separately.

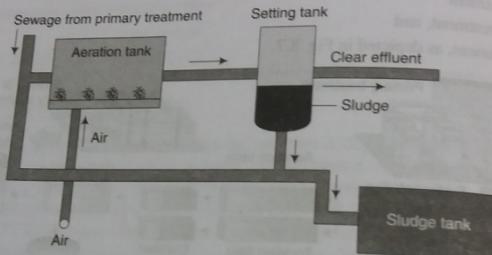
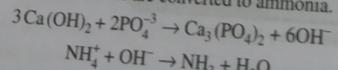


Fig. 8.8 Activated sludge process

8.7.3 Tertiary Treatment

Tertiary treatment involves further purification. It involves the following steps of removing dissolved salts, colloidal particles, gases etc.

- (i) *Removal of phosphate* is done by adding lime. A precipitate of calcium phosphate is formed. Ammonium salts are converted to ammonia.



- (ii) *Coagulation and sedimentation:* Dispersed colloidal forms of fine particles are coagulated in a sedimentation tank by the addition of alum or FeSO_4 . The highly charged Al^{3+} and Fe^{2+} ions neutralise the charge on the colloidal particles. $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_2$ formed as flocculant precipitates bring down the coagulating colloids.
- (iii) *Filtration:* The water is passed through conventional filter beds filled with gravels, coarse sand and fine sand to remove the last traces of suspended matter.

- (iv) *Degassing:* number
 CO_2
(v) *Distillation:*

8.8 POTABLE WATER

Drinking water is contaminated whether it is a disease bearing Unpolluted

8.8.1 Water purifications

human consumption
minerals
quality standards
disinfection
re-contamination

Thermal

1.

2.

3.

1. Primary

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

(i)

(j)

(k)

(l)

(m)

(n)

(o)

(p)

(q)

(r)

(s)

(t)

(u)

(v)

(w)

(x)

(y)

(z)

- (ii) **Degasification:** Dissolved gases are moved by trickling the water through a tall tower filled with a number of perforated hot plates. A large surface area and heat liberates the dissolved gases like NH_3 , CO_2 , H_2S , etc.
- (iv) **Disinfection:** Harmful pathogenic bacteria are removed either by passing Cl_2 gas or ozone or UV light through the water.

8.8 POTABLE WATER

drinking water is water that is intended to be drunk by humans. Water of sufficient quality (free from contaminants) to serve as drinking water or water that is safe for human consumption is called potable water whether it is used as such or not. Although many fresh water sources are drinkable by humans, they may be disease bearing or cause long-term health problems if they do not meet certain water quality guidelines. Unpolluted water is not harmful for human beings and is called safe water or potable water.

8.8.1 Purification of Municipal Water

Water purification is the removal of contaminants from raw to produce drinking water that is pure enough for human consumption. Substances that are removed during the process include bacteria, algae, viruses, fungi, minerals, and man-made chemical pollutants. Many contaminants can be dangerous—but depending on the quality standards, others are removed to improve the water's smell, taste, and appearance. A small amount of disinfectant is usually intentionally left in the water at the end of the treatment process to reduce the risk of re-contamination in the distribution system.

There are three principal stages in water purification:

1. **Primary treatment** – Collecting and screening including pumping from rivers and initial storage.
2. **Secondary treatment** – Removal of fine solids and the majority of contaminants using filters, coagulation, flocculation and membranes.
3. **Tertiary treatment** – Polishing, pH adjustment, carbon treatment to remove taste and smells, disinfection, and temporary storage to allow the disinfecting agent to work.

1. Primary Treatment

- (a) **Pumping and containment:** The majority of water must be pumped from its source or directed into pipes or holding tanks. To avoid adding contaminants to the water, this physical infrastructure must be made from appropriate materials and constructed so that accidental contamination does not occur.
- (b) **Screening:** The first step in purifying surface water is to remove large debris such as sticks, leaves, trash and other large particles which may interfere with subsequent purification steps. Most deep ground water does not need screening before other purification steps.
- (c) **Storage:** Water from rivers may also be stored in bank side reservoirs for periods between a few days and many months to allow natural biological purification to take place. This is especially important if treatment is by slow sand filters. Storage reservoirs also provide a buffer against short periods of drought or to allow water supply to be maintained during transitory pollution incidents in the source river.
- (d) **Pre-conditioning:** Waters rich in hardness salts are treated with soda-ash to precipitate out calcium carbonate utilizing the common ion effect.
- (e) **Pre-chlorination:** In many plants the incoming water used to be chlorinated to minimise the growth of fouling organisms on the pipe-work and tanks. Because of the potential adverse quality effects (see Chlorine below), this has largely been discontinued.

