EVS

Unit-II

2.12 Determination of COD, BOD, DO & Trace Elements

Chemical Oxygen Demand (COD)

Chemical Oxygen Demand is more scientific than the Biological Oxygen Demand. It is a readily measurable parameter for streams and industrial wastes.

Definition

COD is defined as the amount of oxygen required for the chemical oxidation of organic matter in a water sample using strong chemical oxidizing agents, such as potassium dichromate, potassium permanganate, etc.

COD Test

The determination of COD is carried out by the following procedure:

(i) A known volume of the sewage sample is refluxed with a known volume of standard $K_2Cr_2O_7$ and sulphuric acid for 2 hours.

(ii) After refluxion, the amount of unreacted dichromate ($Cr_2O^{2-}_7$) is estimated by titrating against standard ferrous ammonium sulphate using ferroin indicator.

(iii) A blank titration is carried out using distilled water.

Calculation

Volume of std. ferrous ammonium sulphate required for blank $= V_t$ ml

Volume of std. ferrous ammonium sulphate required for sample water $= V_2$ ml

Normality of ferrous ammonium sulphate $= XN$

$$\text{COD mgL-1} \quad \frac{V_1 - V_2}{\text{Volume of sewage}} \times 8 \times 1000\,\text{ppm}$$

Significance of COD

(i) COD is very much needed for the design of treatment plants and management.

(ii) It is used in calculating the efficiency of treatment plants.

(iii) It is used in proposing standards for discharging domestic effluents in various types of water streams.

Biological Oxygen Demand

Both organic and inorganic matters are present in sewage water. Oxygen is needed for the oxidation of these matters. The demand of oxygen by the organic matter is known as Biological Oxygen Demand. It is abbreviated as BOD.

Definition

BOD is defined as the amount of free oxygen required for the biological oxidation of organic matter over a period of 5 days at

20°C. It is called 5-day BOD. It is expressed in milligrams oxygen per litre of water (mgL^{1}) or in ppm.

BOD Test

The determination of BOD is carried out by the following procedure:

(i) A known volume of sewage sample is diluted with a known volume of water, whose dissolved oxygen content is already known.

(ii) The diluted sewage is incubated for 5 days at 20°C in an airtight glass vessel.

(iii) The dissolved oxygen in the sample is determined after the incubation period.

(iv) The loss in oxygen in the sewage is computed as the difference between the original content of oxygen and the residual content of oxygen.

Calculation

$$BOD\ (mgL^{1}) = (DO_b - DOs) / I$$

where,

DO_b = Dissolved oxygen in the blank.

DO_s = Dissolved oxygen in the diluted sample after incubation.

I = Dilution factor.

Factors influencing BOD test

The factors influencing BOD test are,

(i) Types of macroorganism.

(ii) pH value of water.

(iii) Presence of toxic materials.

(iv) Reduced mineral matter.

Significance of BOD

(i) BOD test is the most important test in sewage analysis as it gives the amount of decomposable organic matter.

(ii) It is a measure of strength of the sewage. This test is useful to determine the degree of pollution at any time in the sewage.

(iii) It also helps to find out the amount of pure water required for the dilution of sewage in order to dispose it.

(iv) BOD values are useful in process design and loading calculations, measurement of treatment efficiency and operation and stream pollution control. It also helps in determining the self purifying capacity of a stream.

Trace Elements

Nitrate and Nitrite

As nitrites and nitrates are very hazardous to health, it becomes very essential to monitor their concentrations in water supply regularly. NO_3^- is dangerous to infants of less than six months old as it causes a child disease known as methemoglobinemia. The permissible limit of NO_3^- in drinking water is $10 mgL^{-1}$. Nitrates are the intermediate products obtained both in the oxidation of NH_3 to NO_2 and in the reduction of NO_3^- . The nitrates generally occur in traces in surface water. But their concentration is high in some ground water. NO_3 also occurs in waste water treatment plants, water distribution systems and in natural waters.

Determination

Determination of total nitrite and nitrate is done by reducing them to NH_3 by Devarda's alloy (50% Cu, 45% Al, 5% Zn) in strong alkaline solutions. The ammonia is distilled into excess of standard acid. It is then estimated by spectrophotometric method or titrimetric method.

Cyanide

Free cyanide (CN^- (or) HCN) is highly toxic. Cyanide enters into water bodies through various industrial processes, such as metal refining and cleansing, coke ovens, electroplating, etc. Cyanide can be estimated either by titrimetric method, spectrophotometric or ion selective electrode method.

Sulphate

Sulphate occurs in natural waters. Its concentration may range from a few to several thousand milligrams per litre. Due to pyrite oxidation, the mine drinage waste contains high concentration of sulphate. Excess of Na_2SO_4 and $MgSO_4$ should not be present in drinking water as they cause cathartic action.

The presence of sulphate may be estimated either titrimetrically or gravimetrically.

Gravimetric method

Sulphate is precipitated as $BaSO_4$ in acidic medium (HCl) using $BaCl_2$. The precipitation is carried out near to boiling temperature. The precipitate obtained is digested, filtered and washed with hot water to remove Cl^- ions. Finally, the precipitate is ignited and weighed as $BaSO_4$.

Sulphide

Sulphide is present in ground water, particularly in hot springs. It is also present in common wastewater coming from the decomposition of organic matters, numerous industrial effluents and from reduction of sulphates. H_2S is highly toxic. It causes health of workmen in sewers. It also causes corrosion of concrete sewers.

Sulphide can be estimated by titrimetric method.

Phosphate

Phosphate occurs in natural and wastewaters. It is used for laundry purposes. It is also used for the treatment of boiler water and agricultural land. The run-off from these sources enters into water bodies. Phosphate can be determined spectrophotometrically.

Fluoride

Fluoride is present in all natural water supplies. Fluoride is beneficial if its concentration is below 1 ppm. If the concentration exceeds 6 ppm, it causes cavities in the teeth of young children.

Excess of fluoride causes mottling of teeth or dental fluorosis. If its concentration exceeds 1.0 mg L^1, bone flourosis or crippling effects are observed. Fluoride can be determined by spectrophotometric or ion selective electrode method.

Chromium (VI)

Chromium enters water bodies through discharges from various industries. The normal level of Cr (Vl) in drinking water is 3 to 40 ppm. It's permissible level is 50 ppm.

Chromium can be estimated by titrimetric, potentiometric and spectrophotometric methods.

Lead Lead is highly toxic to humans. It is a serious cumulative body poison. Lead enters water bodies from industrial, mine and smelter discharges.

It is determined by spectrophotometric, polarographic and AAS methods.

Mercury

Mercury is known for its toxic effect. It is very essential to monitor the presence of mercury regularly. The permissible limit of mercury in drinking water is 2ppm.

The best method of determination is flameless atomic absorption method.

Cadmium

Cadmium is highly toxic. It is responsible for several food poisoning. It enters water through industrial discharges or the deterioration of galvanized pipes. Even small quantities of cadmium can cause adverse effect in the arteries of human kidneys. When its concentration is more than 200ppm, it affects certain fishes. The normal level of Cd in potable water ranges from 0.4 to 60 ppm.

It is estimated by spectrophotometric, atomic absorption spectrophotometric and polorographic methods.

Silver

Silver is not a toxic metal. But it causes pathological changes in the kidneys, liver and spleen of rats when the concentration range is between 0.4 and 1 ppm. The normal level of Ag in drinking water is up to 2ppm. The permissible limit is 50ppm.

5. Soil erosion can be minimized by reforesting critical and important water sheds.

6. The runoff and infiltration of manure from animal feedlots may be controlled by improving manure control and planting buffer zones.

7. Proper and complete treatment of sewage water from sewage treatment plants has to be carried out.

8. Proper treatment must be given to all the effluents from the industries.

9. The use of toxic chemical and hazardous materials in the industries should be reduced or eliminated.

10. Use of recycled materials can minimize the pollution. Because the pollution during its production can be avoided by using the recycled materials.

11. By preventing ground water contamination.

12. By reusing treated water for irrigation purposes.

13. By reducing poverty and birth rates.

2.4 Soil Pollution ✓ Unit II / EVS

2.4.1 Introduction

Soil is one of our most fundamental and precious resources. Like clean air and water, life cannot survive without healthy soil. About 95% of our food comes from the land. Soil is the thin layer of organic and inorganic materials that covers the Earth's rocky surface. The organic portion of soil is derived from the decayed remains of plants and animals. These are concentrated in the dark uppermost layer which is called as "topsoil." The inorganic portion is made up of rock fragments. Physical and chemical weathering of bedrock over thousands of years causes formation this inorganic portion.

Definition

Soil pollution is defined as the introduction of substances, biological organisms, or energy into the soil, resulting in a change of the soil quality, which is likely to affect the normal use of the soil or endangering public health and the living environment.

2.4.2 Sources of Soil Pollution

Soil pollution may be caused by various sources. These are

1. Urban wastes
2. Industrial wastes
3. Agricultural practices
4. Soil conditioners
5. Farm house wastes
6. Radioactive wastes
7. Biological agents

1. Urban wastes

Both domestic and commercial wastes are classified as urban wastes. All solid wastes of urban wastes are commonly termed as 'refuse' which contains garbage, and rubbish materials like papers, fibers, plastics, glasses, bottles, street sweepings, leaves, abandoned vehicles and other discarded products.

2. Industrial wastes

More quantity of solid as well as liquid wastes is discharged by most of the industries on soil. The industrial wastes are the major source of soil pollution. Industrial wastes mainly consist of organic and inorganic compounds along with non-biodegradable materials. Because of the filtering capacity of the soil, most of the chemicals present in the liquid wastes are accumulated in the soil and causes soil pollution. These chemicals change and deteriorate the characteristics of the soil and its fertility.

Some of the major industries and their contaminants in soil are shown below in table (Table 2.7)

Table 2.7 Industries Vs Contaminants of Soil Pollution

Industry	Contaminants
Paper mill	Chloride, Sodium
Sugar	Nitrogen, Phosphorous
Steel and Coke	Cyanide, Phenols
Refineries	Phosphate, sulphur, chromium, phenol
Fertilizers	Chloride, Nitrogen, Phosphorous, Pottasium
Pesticides	Organic nitrogen, sulphate

3. Agricultural practices

Agricultural practices carried out now days are the other major sources of soil pollution. Plants on which we depend for food are under attack from insects, fungi, bacteria, viruses, rodents and other animals. They must compete with weeds for nutrients also. In the modern agricultural practices, insecticides, fungicides herbicides nematicides, miticides, rodenticides and molluscidies are used to protect the plants. This causes accumulation of the chemicals in the soil.

Unwanted weeds growing in the field also take nutrients from the soil. The chemical weedicides are used on the field to get rid of the weeds. Chemical pesticides are used by the former to protect the crops from pests and diseases. However some pests and diseases have the ability to resist the chemical sprays. So, in time, the fanner needs to spray the crops with stronger pesticides. Such application of chemicals such as aldrin, endrin, dieldrin endosulphan, B.H.C and D.D.T causes soil contamination and makes entry into the food chain. Its accumulation in the food chain from the lower to the higher tropic level causes more effects and disturbs the entire environment through food chain.

4. Soil conditioners

The soil conditioners are used to increase the fertility of soil. Generally, these contain toxic metals such as Arsenic, Cadmium, Lead, Mercury, etc.

5. Farm house wastes

Increase in population of cows, cattle, pigs and poultries in the farm house result: pollution of soil. Their fecal matter mainly consists of phosphate and nitrate which causes undesirable effects in the soil texture.

6. Radioactive wastes

Generally storage and disposal of radioactive wastes causes penetration and accumulation of radioactive materials and causes soil pollution. The radio nuclide such as isotopes of Strontium-90, Iodine-129 and 131, Caesium-137, Ruthenium-106, Barium-140, Caesium-144 and Lanthanium-140 deposit in the top soil and emit gamma radiations.

7. Biological agents

Soil gets large quantities of human, animals and birds excreta, which constitute the major source of soil pollution by biological agents. The pathogenic organisms that pollute the soil may be classified into three categories. These are:

a. Pathogenic organisms occurring in contaminated soil

b. Pathogenic organisms excreted by man

c. Pathogenic organisms excreted by animals.

2.4.3 Effects of Soil Pollution

1. Removal of the top soil of land causes low fertility for crop production.
2. Disposal of industrial effluents and domestic wastes on land causes accumulation of chemicals and loss of fertility.
3. Presence of arsenic (Ar) in the soil causes chronic poisoning which leads to loss of appetite and weight, diarrhea, gastro intestinal problems and sometimes skin cancer.

4. Soil flora and fauna may be adversely affected.
5. The crop produced in a polluted land will be of inferior quality.
6. Deforestation is threatening not only the existence of many species and the livelihood of many people, but can also influence the climate.
7. Toxic chemicals leached from land filling areas into the soil underneath cause large number of birth defects, cancers and respiratory, nervous and kidney diseases.
8. The disposal of cadmium from mining, metallurgy, chemical and electroplating industries cause chronic poisoning, formation of kidney stones and sometimes failure of kidneys.
9. Accumulations of methyl mercury compounds are much more toxic than other forms of mercury. It causes neurological problems and damages renal glomeruli and tubules.

2.4.4 Control of Soil Pollution

Soil pollution can be controlled by adopting three R's: Reduce, Reuse and Recycle. This would give us less solid waste. The following measures may be adopted to control soil pollution.

a. Preserving the top soil which is the fertile soil. By planting of more trees soil erosion can be controlled.
b. Understanding the relationship between soil, water and plant and protect the mineral cycles of fixation.

c. Disposal of properly treated industrial wastes, physically, chemically and biologically causes fewer hazards.

d. Preventing the entry of leachates from the landfills into the soil layer can minimize the entry of chemicals.

e. Use of fertilizers and pesticides preferable in optimal dose.

f. Crop rotation can increase the yield of crops.

g. More plough or mix can improve aeration, porosity and permeability of soil.

2.5 Thermal Pollution

2.5.1 Introduction

Temperature of water is an important water quality parameter. Warm water can be found in a number of different areas in nature such as, hot springs or water warmed by volcanic activity. However, the warm water created by man and introduced into nature can become a problem. The temperature of the water affects many physical, biological and chemical characteristics of a river or lake. Cool water can hold more oxygen than warm water because gases dissolve easier in cooler water.

Definition

Thermal pollution can be defined as 'the excessive raising or lowering of water temperature above or below normal seasonal ranges in streams, lakes or estuaries or oceans as the result of discharge of hot or cold effluents into such water'.

2.5.2 Sources of thermal pollution

Thermal pollution may be caused by four major sources. They are:

a. Water as a cooling agent.

b. Soil erosion.

c. Deforestation of shorelines.

d. Run-off from hot paved surfaces.

a. Water as a cooling agent

It is the major source of thermal pollution of water in most part of the world. The use of water as a cooling agent in power plants (natural gas, coal or nuclear) and factories and industrial facilities causes thermal pollution.

The power plants and industries withdraw water from a nearby water source for cooling the machineries and return the heated water to the same water body. This cheap method of cooling is mostly used by many industries. The discharge of hot water into water bodies, like streams, rivers, lakes and oceans causes the thermal pollution.

b. Soil erosion

Soil erosion makes the water muddy, which in turn increases the absorption of light, thus increasing the water temperature.

c. **Deforestation of shorelines**

This contributes to the problem of thermal pollution in two ways. First, the plant roots hold soil articles together. Hence the deforestation results erosion of soil particles. Secondly, vegetation provides shade to the water surface. Deforestation increases the amount of light hitting the water surface, thereby raising the water temperature.

d. **Run-off on hot surface**

Storm water runoff on warmed urban surfaces, such as streets, sidewalks and parking lots causes raising of the temperature of water that flows on the surface.

2.5.3 Effects of thermal pollution

Thermal pollution increases the temperature of water considerably. This increase in temperature causes the following effects:

1. **Change in water properties**

Temperature affects physical, biological and chemical parameters in a water body.

2. **Disturbed Ecosystem**

Most aquatic organisms have adapted to survive within a range of water temperatures. Some organisms like trout and stonefly nymphs prefer cooler water, while others such as carp and dragonfly nymphs thrive under warmer conditions. As the temperature of a river or lake increases, cool water species will be replaced by warm water organisms. Few organisms can survive in temperatures of extreme heat or cold.

3. Reduced dissolved oxygen

The addition of heat reduces the water's ability to hold dissolved gases, including the oxygen required for aquatic life. If the water temperature is greater than 95°F, the dissolved oxygen content may be too low to support some species.

4. Increased bacterial growth

Warmer water allows bacterial populations to increase and thrive, and algae blooms may occur.

5. Photosynthesis

The rate of photosynthesis by algae and larger aquatic plants is also affected by thermal pollution.

6. Thermal shock

When a power plant first opens or shuts down for repair, fish and other organisms adapted to a particular temperature range can be killed by the abrupt change in water temperature. This is called as thermal shock.

7. Increase in toxicity:

The rising temperature increases toxicity of the chemicals present in water which causes massive mortality of fishes.

2.5.4 Control of thermal pollution

Following are some of the preventive measures of thermal pollution:

- Temperature of water can be reduced by taking the water to wet or dry cooling towers which are being used to precool that water before discharge transfers the heat from the water to the atmosphere.
- Discharging the heated water into shallow ponds or canals, allowing it to cool, and reusing it as cooling water.
- The thermal discharges from an industry can also be used in heating homes, building or other such structures. This is achieved by circulating the hot water through pipes in the structures.
- Water with temperature can be successfully used in aquaculture.
- The heated water can also be used in agriculture, especially for frost protection during the cold seasons.

2.6 Radioactive Pollution

2.6.1 Introduction

An atom is characterized by its atomic number and atomic mass. Carbon is one of the most frequently occurring chemical in living materials which is not radioactive. It has exactly 12 atomic mass units. Other atoms are measured in relation to Carbon-12. Carbon-14 has two extra neutrons in its nucleus has the ability of radioactive.

Hydrogen has an atomic number of 1 and an atomic mass of 1. Isotopes of hydrogen have the same atomic number but a higher atomic mass. Hydrogen-2 or deuterium is an isotope of hydrogen. It has an atomic number of 1 and an atomic mass of 2. It is not radioactive. The increased atomic mass is due to an added neutron in the nucleus. Deuterium is in the 'heavy water' used in the nuclear reactors. Hydrogen-3, called tritium has the ability of radioactivity. It consists of two neutrons and a proton in the nucleus. It is produced in a nuclear reaction.

When radium 226 decays, it loses a positively charged alpha particle from its nucleus. An alpha particle has two protons and a mass of 4 atomic units. Loss of the alpha particle changes radium 226 into another element, called radon 222. Radium 226 is a radioactive solid under normal conditions, where as radon 222 is a radioactive gas. Loss of one or more protons changes the chemical element into a different chemical. Absorption or loss of a neutron gives an isotope of the same chemical since chemical properties are determined by the number of protons and electrons in an atom.

Nuclear reactors are used to generate power by using nuclear fuel. Uranium and its isotopes are mostly used in all the nuclear reactors. Generally, Uranium-235 and Uranium-238 are used in the nuclear reactors for power generation. Ur-235 alone and along with Ur-238 is used in light- water reactors and heavy-water reactors respectively.

2.6.2 Sources of nuclear pollution

Initially the Uranium is extracted from ores. It is refined in chemical process and it is fabricated into fuel rods. These fuel rods are inserted into the nuclear reactor. Generally, the rods are kept in the reactor for a period of about two years. During that period, they become intensely radioactive due to the production of fission products and formation of elements like plutonium, americium and curium.

The vast majority of highly radioactive wastes are generated from commercial nuclear power reactors. Highly radioactive wastes contain two types of wastes.

1. Solid irradiated nuclear fuel assemblies (generally called "spent" or "used" fuel rods)and
2. Liquid high-level radioactive wastes resulting from the "reprocessing" (extraction of fissile plutonium and uranium) of solid irradiated fuel rods.

Irradiated nuclear fuel rods discharged from commercial nuclear power plants are highly radioactive, a million times more so than when they were first loaded into a reactor core as "fresh" fuel. If unshielded, irradiated nuclear fuel just removed from a reactor core could deliver a lethal dose of radiation to a person standing three feet away in just seconds. Even after decades of radioactive decay, a few minutes unshielded exposure could deliver a lethal dose. Certain radioactive elements (such as plutonium-239) in "spent" fuel will remain hazardous to humans and other living beings for hundreds of thousands of years. Other radioisotopes will remain hazardous for millions of years.

Highly radioactive wastes are dangerous and deadly wherever they are, whether stored at reactor sites (indoors in pools or outdoors in dry casks); transported on the roads, rails, or waterways; or dumped.

Low-level waste includes items that have become contaminated with radioactive material or have become radioactive through exposure to neutron radiation. Contaminated cloths, protective shoe covers, wiping rags, mops, filters, reactor water treatment residues, equipments and tools, luminous dials, medical tubes, swabs, injection needles, syringes, and laboratory animal carcasses and tissues are the typical examples of low level wastes.

Pollution from mining

Pollution created from mining of uranium is the important in considering the whole nuclear fuel-cycle. Near the uranium mining areas, the locally available rivers are seriously polluted due to poor tailings management. In due course, the situation has been largely overcome but there have still been occurrences of tailings-pond failures. In all mining operations this is a lifelong problem. This problem needs constant caution.

Mill tailings wastes

These are the residues remaining after the processing of natural ore to extract uranium and thorium. Disposal of dry uranium tailings causes release of radioactive radon gas but in amounts that would not add significantly to the exposures of surrounding communities. Radon is constantly being released from all soil, especially when it is disturbed by ploughing.

Nuclear Power Stations

Nuclear-electric power stations release radioactive materials to air and water in amounts small enough not to harm the environment. The most obvious environmental effects that nuclear reactors do not cause are those resulting from combustion.

Coal-fired plants

Coal-fired plants also emit more radiation. In certain cases, the radioactive emissions from a coal-fired plant can be as high as, or even higher than, those from a nuclear plant. The radioactive emission depends on source of the coal and its impurities. Very little amount of uranium and thorium are present in coal. At the time of decaying these elements produce radium and radon. These decaying elements are disposed into the environment either from the chimney of the plant or disposed through the ash. Also this radioactive element causes the ground water pollution by leaching.

2.6.3. Effects of Radioactive Pollution

The nuclear pollution affects both the biotic and abiotic components of the environment. Its effect depends on the nature of radiation, level of radioactivity and the extent of the radiation.

The low level radioactive materials pose no risk at all, but can still be detected by radiation instrumentation, thereby being more of an annoyance than a threat. In the case of low-level contamination by isotopes with a short half-life, the best course of action may be to simply allow the material to naturally decay. Longer-lived isotopes should be cleaned up and properly disposed of.

High level of radiation poses major risks to people and the environment. The high level radiation affects the living beings in both externally and internally. Radioactive contamination can enter the body through ingestion, inhalation, absorption, or injection. Because of this reason, it is important to use personal protective equipment when working with radioactive materials. Radioactive contamination may also be ingested as the result of eating contaminated plants and animals or drinking contaminated water or milk from exposed animals.