WATER TREATMENT AND ANALYSIS

UNIT – I

1.1 Introduction - Characteristics of water - Alkalinity - Hardness - Unit of hardness – Total solids - Oxidation - Transparency - Silica content.

1.2 Purification of Water for drinking purpose - Potability of water – Clarification - Coagulation - Contact and Electrochemical Coagulation.

1.3 Sterilization and Disinfection of water - Precipitation - Aeration - Ozonisation - Chlorination.

1.1. INTRODUCTION

Water is not only essential for human beings, plants and animals for sustaining life but is also equally important for agricultural, industrial and other purposes. The important sources of water are surface water, underground water and rain water. The increasing population in urban areas results in concentrated discharge of large quantities of water into rivers, lakes and estuaries. This results in the purifying capacity of the receiving water being overtaxed, resulting in gross pollution, severe nuisance and far reaching economic and health consequences. The concern is shown not only by experts and agencies dealing with the problem of pollution but by the public at large. Water is one of the abundant available substances in nature. Water forms about 75% of the matter on earth's crust. It is an essential ingredient to both plant and animal life. Moreover, it also enjoys a unique position in industries

CHARACTERISTICS OF WATER

As per the suggestion given by world health organization (WHO) and by Indian council of medical research (ICMR), the followings are the important characteristics of portable water.

- It should be clear, colorless and odorless.
- It should be cool and pleasant to taste.
- It should be free from harmful bacteria and suspended impurities.
- It should be free from dissolved gases like CO_2, H_2S, NH_3 etc., and poisonous minerals like lead, arsenic, manganese, etc.,
- Hardness should be less than 500 ppm.
- Chloride content should be less than 250 ppm.
- Fluoride content should be less than1.5 ppm.
- Total solid content should be less than 500 ppm.
- PH of the portable water should be 6.5 to 8.5.

ALKALINITY

Definition

Alkalinity of water is a measure of its acid neutralizing ability or it is the tendency of water to accept H^+ ions in order to neutralize it with the supply of OH^- ions. In water analysis, it is often desirable to know the kinds and amounts of the various forms of alkalinity present in water.

Unit*:* ppm of $CaCO_3$.

Sources:

Alkalinity in water is due to the presence of bicarbonates, carbonates and hydroxides of Ca, Mg, Na and K. This type of alkalinity is usually introduced into the water resource by

metallurgical industries, chemical industries, and drainage from abandoned mines and from many other industrial sewages.

Thus, the alkalinity of water may be due to

- Hydroxide only
- Carbonate only
- Bicarbonate only
- Both hydroxide and carbonates
- Both carbonates and bicarbonates.

The possibility of hydroxide and bicarbonate existing together in water is ruled out because they combine with each other to form carbonate.

$$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O$$

Classification

1. Bicarbonate alkalinity
2. Carbonate alkalinity
3. Hydroxide alkalinity

Sanitary Significance

- High alkalinity in natural water favors the growth of algae and phytoplankton. Usage of this alkalinity water may cause some effects on human beings.
- It is used in evaluating the buffering capacity of waste waters and sludges.
- Determines the suitability of water for irrigation.
- Provides an idea of the nature of salts present.
- It indicates the corrosion extent of the water.
- Used in removal of ammonia in air striping.
- In Water softening

Removal of alkalinity

Alkalinity in water, can be removed by adding limited amount of HCl.

Alkalinity measurements*:*

Alkalinity may be determined by potentiometric method or using pH meter or titrimetric using different acid base indicators. Out of these methods, determination of various types and amounts of alkalinity is easily carried out by titration with standard hydrochloric acid employing phenolphthalein and methyl orange as an indicator separately or in succession.

Estimation of alkalinity

Titrimetric method is preferred using phenolphthalein and methyl orange as indicators.

Principle:

Alkalinity of a given water sample can be obtained by neutralizing the hydroxide, carbonate and bicarbonate ions with standard acid, using phenolphthalein and methyl orange as indicators. The phenolphthalein end point at pH 8.3 indicates the complete neutralization of hydroxide ions and half of carbonate ions. Further, titration upto the methyl orange endpoint indicates the neutralization of total alkalinity due to hydroxide, carbonate and bicarbonate ions.

$OH^- + H^+ \rightarrow H_2O$ ----- (1) Phenolphthalein

$CO_3^{2-} + H^+ \rightarrow HCO_3^-$ ----- (2) pH = 8 to 9

$HCO_3^- + H^+ \rightarrow H_2O + CO_2$ ----- (3) Methyl orange

The end point with phenolphthalein (P) indicator indicates the completion of reaction (1) and (2). Whereas the total volume of the standard acid used from the beginning upto the methyl orange end point (M) corresponds to the completion of reaction (1), (2) (3).

From the above, following conclusions may be drawn

- When P=0, both OH^- & CO_3^{2-} are absent.
- When P=M, the sample consists of only OH^- ions.
- When P= (1/2) M, the sample consists of only CO_3^{2-}.

$$CO_3^{2-} + H^+ \; HCO_3^- \rightarrow HCO_3^- + H^+ \; H_2O + CO_2$$

- When P> (1/2) M, the sample consists of OH^- and CO_3^{2-}.
- When P< (1/2) M, the sample consists of HCO_3^- and CO_3^{2-}.

Hard water and soft water

Hard water

Water which does not produce lather with soap solution, but produce while precipitate (scum) is called hard water.

This is due to presence of dissolved Ca and mg salts.

$$2C_{17}H_{35}COONa + Ca^{++} \rightarrow (C_{17}H_35COO)_2Ca + 2Na^+$$

Sodium soap water hardness causing ion calcium soap water insoluble

Soft water

Water, which produces lather readily with soap solution is called soft water.

This is due to the absence of Ca &Mg salts.

How to detect hardness?

Hardness of water can be detected in two ways,

1. When the water is treated with soap solution, if it prevents lathering and form white scum, the water contains hardness.
   $2C_{17}H_{35}COONa + CaCl_2 \rightarrow (C_{17}H_35COO)_2Ca + 2NaCl$
   Soap hardness causing sub hard soap
2. Water containing hardness, gives wine red colour with EBT indicator at pH of 9-10.

HARNESS OF WATER

Hardness is the characteristic of water which does not give good lather with soap. This property of water is due to the presence of bicarbonates, chlorides and sulphates of calcium, magnesium and other salts.

Classification of Hardness of Water

Hardness of water can be classified into two categories.

1. Temporary hardness (or) Carbonate hardness.
2. Permanent hardness (or) Non-Carbonate hardness.

1. Temporary (or) Carbonate hardness

This is caused by the presence of dissolved bicarbonates of calcium and magnesium. Temporary hardness is mostly destroyed by mere boiling of water. During boiling, the bicarbonates are decomposed and form insoluble precipitates. Carbonates and hydroxides can be removed by filtration, while CO_2 escapes out.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

Insoluble

$$Mg(HCO_3)_2 \rightarrow Mg(OH)_2 + 2CO_2$$

Insoluble

2. Permanent (or) Non-Carbonate hardness

This is due to the presence of dissolved chlorides and sulphates of calcium and magnesium. Unlike temporary hardness, permanent hardness is not destroyed on boiling.

Total Hardness of Water = Carbonate Hardness + Temporary Hardness + Permanent Non-Carbonate Hardness hardness

Units of Hardness

Parts per million (ppm)

It is the number of parts of calcium carbonate equivalent hardness per million (10^6) parts of water. 1 ppm = 1 part of $CaCO_3$ equivalent hardness in 10^6 parts of water.

Milligram per Litre (Mg/L)

It is the number of milligram of $CaCO_3$ equivalent hardness present per litre of water. 1 mg/litre = 1 mg of $CaCO_3$ equivalent hardness in 1 litre of water

Clarks degree (°Cl)

Cl-degree clerk is the number of parts of calcium carbonate equivalent hardness per 70000 parts of water. 1ppm = $0.07^0 Cl$.

French degree (^{0}Fr)

^{0}Fr- degree French is the number of parts of calcium carbonate equivalent hardness per 10^5 parts of water. 1ppm=0.1^0Fr

Total solid content

It is the amount of non- volatile substances present in water. Generally it is expressed in mgs/kg.

Determination

Total solid content of natural water is determined by converting Ca and Mg bicarbonates into their corresponding carbonates.

$$Ca(HCO)_2 \rightarrow CaCO_3 + Co_2 + H2O$$

$$Mg(HCO_3)_2 \rightarrow MgCO_3 + CO_2 + H2O$$

Other type of solids

In addition to the total solids, the following three other type of solids are also present.

- **Fixed residue solids**

It is produced by combining the total solids for several minutes at 1073K. during which their mass will diminish, due to removal of organic substances, evaporation of moisture and decomposition of carbonates etc.,

- **Minerals residue solids**

It is the quantity obtained by adding up all the cations and anions including $Co_3^{2-,}$ Al_2O_3, Fe_2O_3 and SiO_2 in water.

- **Sulphate solids**

If the total solids are treated with sulphuric acid, all the cations present in water are converted into sulphates, the total mass obtained is called sulphate solids.

Oxidation

Contamination of water by the organic substances is expressed by oxidability.

Oxidability is the amount of oxygen (in mgs) required to oxidise the organic compounds present in 1 kg of water.

Unit of oxidabiliy mgs/ kg

Transparency

It represents the conc. Of suspended solids. It is determined by weight method and type method. The familiar method is type method.

In this method the height (cm) of a column of water in a glass tube, through which it is still possible to distinguish printing.

Silica content

The conc. Of silicic acid (H_2SiO_3) present in natural water is expressed as silica content. It ranges from 8-10 to 90 mgs/lit in natural water.

In problem is operating power generation equipment, deposition of silicate scale will affect the operation. The presence of silicic acid affect the dislocation process because silicic acid reacts in the ion exchange process. It is removed by using ion exchangers.

1.2. PURIFICATION OF WATER FOR DRINKING PURPOSE

Water is an essential ingredient of animal and plant life, generally municipal water is used for drinking purpose and hence water conditioning and waste water treatment is essential. The treatment of water to which it is subjected, depends on the purpose for which the treated water is used.

Hard water, containing dissolved Ca and Mg salts. Forms scales in boilers, which act as thermal insulations, so the water, used for boilers, must be free from Ca and Mg salts.

Objective of the treatment

- To remove colour, taste and odour.
- To remove dissolved gases, impurities and harmful minerals.
- To remove organic impurities.
- To remove pathogenic bacteria.
- To make water safe for drinking and domestic purpose.

Potability of water

The word portable comes from the latin word potate means to drink. Thus portable water is know thing but drinking water. It is safe to drink and to use for food preparation.

Potability of water

It is the ability to convert the given water into drinking water.

Clarification

The process of removal of coarse, dispersed and colloidal impurities from water is known as clarification. Clarification can be done in two ways.

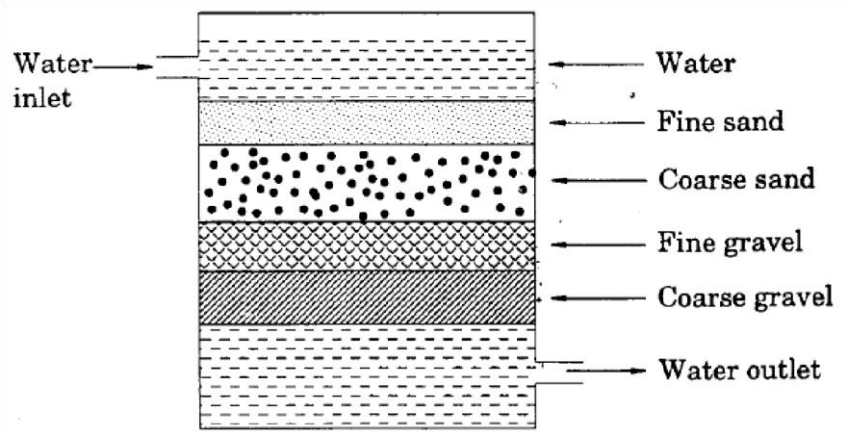
1. Sedimentation
   It is a process of removing suspended impurities by allowing the water to stand undisturbed for 2-6 hrs in a big tank. Most of the suspended particles settle down at the bottom, due to forces of gravity, and they are removed. Sedimentation removes only 75% of the suspended impurities.

Objectives of sedimentation

- Suspended and colloidal impurities are separated.
- The particles having specific gravities greate than 1.20 settle down.
- Settling of particles depend on velocity of flow, size and specific gravity of particles.
- Size and shape of particles are increased by precipitation by adding coagulation.

2. Filtration

It is process of removing bacteria, color, taste, odour and suspended impurities etc., by passing the water through filter beds containing fine sand, corase sand and gravel. A typical sand filter is shown below.



The sand filter consists of a tank containing a thick top layer of fine sand followed by coarse, fine gravel and gravel coarse. When the water passes through the filtering medium it flows through the various beds slowly. The rate of filtration decreases slowly due to the clogging of impurities in the pores of the sand bed. When the rate of filter becomes very slow. The filtration is stopped and the thick top layer of fine sand is scrapped off and replaced with clean sand. Bacterias are also partly removed by this process.

Coagulation Principle:

The suspension of particles in water is stabilized by the mutual repulsion of like charges on the particles. Neutralization of these charges by coagulants (i.e. with high valence ions) results in coalescence.

Coagulants:

These are positively charged molecules of relatively low molecular weight. With water these form an insoluble gelatinous precipitate. It adsorbs and entraps very fine suspended impurities forming bigger flocs, which settles down easily. Example: Alum, Ferrous sulphate. Impurities that can be removed

- Colloids
- Finely divided silica
- Fine clay particles

Example

Aluminium sulphate used only in high alkaline waters. (OR) water is pretreated with lime. The Aluminium sulphate reacts with OH^- to form the Aluminium hydroxide, which is a gelatinous precipitate.

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2SO_4$$

Gelatinous precipitate adsorbs and entraps very fine negatively charged suspended impurities forming bigger flocs, which settles down easily.

COAGULANTS (STUDY MATERIAL)

Sodium aluminate $NaAlO_2$.

(Used in waters with pH range less than 7)

$NaAlO_2 + 2H_2O \rightarrow 2Al(OH)_3 + NaOH$

The aluminium hydroxide flocs cause coagulation. The NaOH precipitates the magnesium salts as $Mg(OH)_2$

$MgSO_4 + 2NaOH \rightarrow Mg(OH)_2 + Na_2SO_4$

Copperas or ferrous sulphate ($FeSO_4 . 7H_2O$)

(Used in waters with pH range of 8.5 or pretreated water with lime.)

$FeSO_4 + Mg(HCO_3)_2 \rightarrow Fe(OH)_2 + MgCO_3 + CO_2 + H_2O$

$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$

Ferric salts are heavier particles which settles down easily.

Activated sludge process

Secondary or biological treatment includes processes such as Activated sludge process. Filtration etc. The main function of secondary treatment is to convert the remaining organic matters of the effluent into stable form by oxidation or nitrification.

Principle

The activated sludge is obtained by settling sewage in the presence of excess oxygen. Thus, activated sludge is that sludge which settles down after the sewage has been freely aerated and agitated for a certain time. The activated sludge is biologically active and contains a large number of aerobic bacteria and other micro-organisms. In Activated sludge process effluent is treated biologically. When the sludge is mixed with effluent, the bacteria in the

activated sludge multiply rapidly. These aerobic bacteria oxidises the organic matters and promotes coagulation and flocculation. They also convert the colloidal and suspended solids into settle able solids.

Process

The effluent is mixed with the required quantity of activated sludge and it is aerated for 4-10hrs. The aerated mixture is sent to secondary clarifier. The matters which settles down is called sludge. The liquid is called effluent. Settled sludge is the activated sludge and a part of it is sent for recirculation. The rest is disposed of for drying beds, dumping into sea etc.

Advantages

- Gives clearly treated liquid free from bad smell or odour
- The degree of purity can be varied depending on the requirements
- No trickling filter flies

Disadvantages

- Skilled supervision and constant check on the return sludge is necessary.
- The process is not efficient in removing all industrial wastes.
- Large volume of sludge presents difficulty in disposal.
- The process gets upset when there is a change in the quality or quantity of water.
- The success depends on mainly the aeration provided.
- The term sludge volume index (SVI) is used to indicate the degree of concentration of sludge. It also indicates the physical state of the sludge.
- Desired SVI is 100ml/g. High value indicates the favorable condition for sludge bulking.

Contact coagulation

It is based on the ability of small particles to adsorb on large particles of sand or suspended precipitate through which water is filtered.

Advantages

More effective clarification

Reduces the time

Electrochemical coagulation

The basic principle of operation is the anode dissolution Al plates when direct current is passed through them. In electrochemical coagulation two Al plates one is connected to the +ve and another to the –ve pole of the powerful source of low voltages. Now the water is passed

between Al plates. When the charge is applied Al, ions pass into the water to form Al $(OH)_3$ this gelatinous aluminum hydroxide entraps the fine suspended particles and settle down.

Advantages

- Stables flasks are formed and precipitated.
- PH of the medium cannot be changed.

Disadvantages

- Energy required is more.

1.3. STERILIZATION (Or) DISINFECTION

The filtered water still contains small amounts of pathogenic (disease producing) bacteria. In order to use this water for drinking purpose, all the pathogenic bacteria and other micro-organisms present in it must be killed.

The process of destroying /killing of pathogenic bacteria and other micro-organisms is called disinfection and the chemicals used for this purpose are called disinfectants. Some of the important methods of sterilization are as follows:

a) Precipitation

b) Aeration

c) Ozonisation

d) Chlorination

a) Precipitation

Minerals deposits are formed by ionic reactions resulting in the formation of an insoluble precipitate.

For example $Ca2+ (aq) + 2HCO3-(aq) \rightarrow CaCO3 (p) + H2O + CO2$

This precipitate known as scale.

b) Aeration

The process of bringing water in contact air is called aeration.

Types of Aeration

This is done either by

- Cascading water through air (OR)
- Passing air through water under pressure.

Construction

Fountains with spraying nozzles are used which effects intimate contact of water and air.

Impurities that can be removed

Deactivating the anaerobic bacteria. Gases like CO_2 and H_2S, which causes bad taste and odour to the water. Removing ferrous and manganous salts as insoluble ferric and magnetic salts. Removes color and odour.

Advantages

- Gives freshness to water
- Increasing the dissolved O_2 content in water.
- Thickens and removes of oil, grease, solid grits and odours

c) Ozonisation

Ozone is a powerful disinfectant and is readily absorbed by water. Ozone is highly unstable and breaks down to give nascent oxygen.

$$O_3 \rightarrow O_2 + [O]$$

The nascent oxygen is powerful oxidizing agent and kills the bacteria. Disadvantages of this process are

- This process is costly and cannot be used in large scale.
- Ozone is unstable and cannot be stored for long time.

d) Chlorination

Chlorine is the most commonly used sterilizing agent in water treatment. It is capable of killing B.Coli and other bacteria. The process of adding chlorine to water is known as chlorination. Chlorine can either be used in the gaseous form or liquid chlorine. Chlorine reacts with water to produce nascent oxygen which destroys the bacteria. Chlorination can be done by the following methods:

- By adding chlorine gas

Chlorine gas can be bubbled in the water as a very good disinfectant

- Chlorine when used directly as a gas liberates nascent oxygen as given below :

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

Hypochlorous acid

$$HOCl \rightarrow HCl + [O]$$

Nascent oxygen

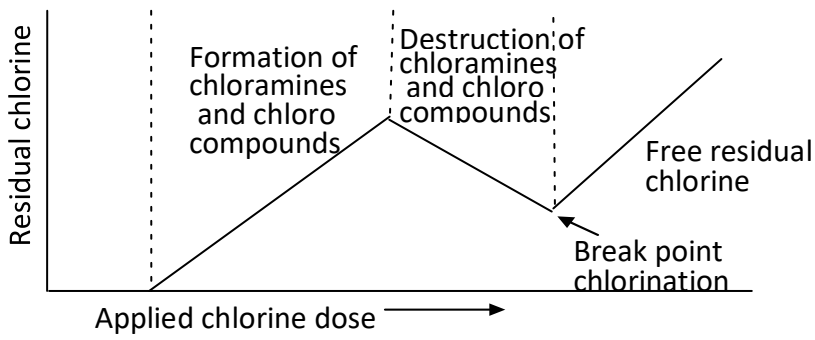
Super Chlorination

The sterilization process involving a large excess of chlorine is called **super chlorination.** Super chlorination not only destroys the microorganisms but also the other organic impurities present in water. The process is usually followed by dichlorination by NH_3 or SO_2.

Break point chlorination

Break point chlorination is a carefully controlled chlorination process in which water is treated with such an amount of chlorine which is just sufficient to destroy bacteria, oxidize organic matter to react with ammonia, if present and to leave behind slight excess of free chlorine.

Chlorine may be added directly as a gas or in the form of bleaching powder. When chlorine applied to water, the results obtained can be depicted graphically as shown in Fig.3.2. The graph shows the relationship between the amount of chlorine added to water and the residual chlorine.



From **Fig** the graph **Break** (**Fig point chlorination curve**) it is clear that **initially** the chlorine added is used to kill the bacteria's and oxidizes all the reducing substances present in the water and there is no free residual chlorine.

On increasing the amount of applied chlorine, the amount of combined residual chlorine also increases. This is due to the formation of chloramines and other chlorocompounds. At one point, on further chlorination, the oxidation of chloramines and other impurities starts and there is a fall in the combined chlorine content. Thus, the combined residual chlorine decreases to a minimum point at which oxidation of chloramines and other impurities complete and free residual chlorine begins to appear, this minimum point is known as "break point chlorination". Thus, the break point chlorination eliminates bacteria's, reducing substances, organic substances responsible for the bas taste and odour from the water.

Reference

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3. https://www.scribd.com/document/23180395/Engineering-Chemistry-Unit-I-Water-Treatment

Questions

Section – A

1. Define alkalinity.
2. Define hardness of water.
3. Write about hard and soft water.
4. What do know about oxidation?
5. Write the objectives of purification of water for drinking purpose.
6. Define sterilization.
7. Write about ozonisation.
8. What is mean by chlorination?

Section – B

1. Explain the types of hardness? How is it removed?
2. Write note on alkalinity and its types.
3. Write notes on transparency and total solid content.
4. Explain electrochemical coagulation.
5. Explain about aeration.
6. Explain the ozonisation.

Section – C

1. Explain the various steps involved in the conversion of water into potable water.
2. Explain the various methods of sterilization.
3. Explain the coagulation process.