Ch.3. water pollution

Ch.2
Water pollution:

Water covers over 70% of the Earth’s surface and is a very important resource for people and the environment. Water pollution affects drinking water, rivers, lakes and oceans all over the world. This consequently harms human health and the natural environment.
water on the Earth’s surface is continually evaporating and forming clouds from which the water returns to the Earth’s surface in the form or rain, hail and snow. This circular movement is called the water cycle.

As is well known ; pure water does not occur in nature. The purest is the rain which falls upon the ocean far from the neighborhood of land. Over the sea and over the land near the sea.

The water for drinking and domestic purposes is generally supplied by rivers , lakes and wells. Such water contain

- salts of calcium, magnesium, potassium, iron and Sodium.
- Organic matter and dissolved gases like CO_2, O_2, N_2 and ammonia.
- Suspended matter also present in natural water , such as fine particles of clay and microorganism.

Sources of water pollutants:

- Domestic waste
- Industrial waste
- Atmospheric
- Soil treatment methods
- Purification methods
- Metal corrosion

Sampling water:

Care should be taken to obtain a sample that is truly representative of exciting conditions. Also the sample recommended to be collected and stored in bottles made of resistant borosilicate glass or hard rubber .

- Before collecting samples from the distribution systems the line should be flushed for sufficient period to ensure that the sample is representative of the supply.

- Sample from wells should be collected only after the well has been pumped for a sufficient time to ensure that the sample will represent the ground water, which feeds the well.

- When the sample are collected from a river or stream the analytical values may vary with depth, stream flow and distance from shore. It is best to take an integrated sample from top to bottom in the middle of the stream.

Physical examination of water:

1- Odor:

- Cold odor quality|:
  Shake about 250 ml samples at 20 in a 500 ml wide mouth flask. The odor may be aromatic, balsamic, fishy earthy vegetable …..etc

- Hot odor quality:
  Pour about 250 ml samples into 500 ml flask closed with glass. Heat the water to about 60°C , and detect any of H_2S, phenol or chlorine.

2- Color:

The expression color shall be defined to mean true color that is the color that is due only to substances which are actually in solution, and not to suspended matter. The suspended matter must be removed by centrifugation of the sample.

Color is determined by visual comparison of the sample with known concentrations of colored solutions.

Chemical examination:

1- Ammonia nitrogen:

Ammonia nitrogen is present in variable concentration in many surface and ground waters, For determination of ammonia two methods used;

1- Distillation Method:

Quantitative recovery of free ammonia nitrogen can be achieved when the distillation mixture is kept near pH 7.4 .So phosphate buffer is added to maintain a constant pH in the sample during the distillation process. After the isolation of ammonia nitrogen ,it treated with Nessler's reagent (K_2HgI_4/NaOH) the product is colored compound has absorbance in the range 400- 500 nm

$$2HgI_4^{2-} + NH_3 \longrightarrow NH_2Hg_2I_3 + NH_4 + 5\ I^-$$

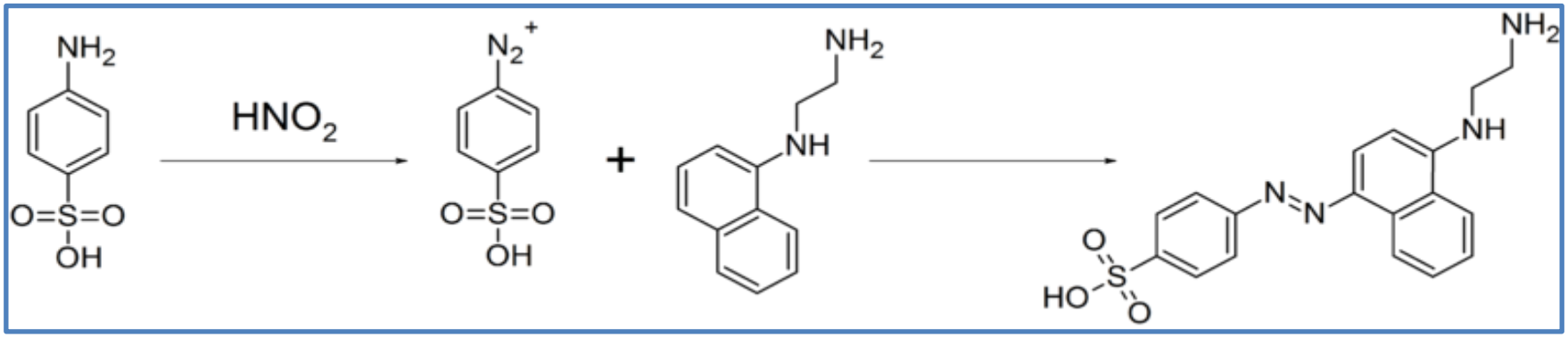
2- Direct Nesslerization method:

With sample that have high content of ammonia , the distillation step is omitted and the sample is nesslerized directly . Pretreatment with $ZnSO_4$ and alkali is used to precipitate Ca, Mg, Fe and sulfide which might cause turbidity with the reagent.

2-Nitrite NO_2^-

Nitrite occurs in water as an intermediate in oxidation or reduction process. In raw surface waters , trace amounts indicate the presence of pollution.

The nitrite concentration is determined though the formation of reddish purple azo dye which has absorbance at 520 nm produced at pH 2 to 2.5 by the coupling of diazotized sulfanilic acic with ∝- naphthylamine hydrochloroide.



3-Nitrate No_3^-

It generally occurs in trace quantities in surface water but may attain high levels in some ground water .The presence of nitrate usually indicates past organic pollution.
Two methods for determination of nitrate are presented below.

1- Phenoldisulfonic acid method:

The basic reaction between nitrate and phenol -2,4-disulfonic acid to produce the alkaline salt which has yellow color measured at 480 nm.
Chloride interfere with determination of nitrate because of their reducing action and would result in serious loss of nitrate . Therefore chloride should be removed by adding Ag_2SO_4 and use NH_4OH to develop the color and avoid precipitation of excess silver ion as $Ag(OH)_2$

2- Reduction method:

This method based on reduction of nitrate to ammonia by means of aluminum foil in an alkaline medium and the determination of the evolved ammonia through Nesslerization reaction.

4- Dissolved oxygen(DO):

Dissolved oxygen is used as an indicator of the health of a water body, where higher dissolved oxygen concentrations are correlated with high productivity and little pollution. Dissolved oxygen in potable water is determined by **winkler Method** .This test is performed on-site, The steps of the method as follow:

First: Manganese(II) sulfate is added to an environmental water sample. Next, Potassium iodide is added to create a pinkish-brown precipitate. In the alkaline solution, dissolved oxygen will oxidize manganese(II) ions to the tetravalent state.

$Mn^{+2} + OH^{-} \longrightarrow Mn(OH)_2$

$2\ Mn(OH)_2(s) + O_2(aq) \rightarrow 2\ MnO(OH)_2(s)$

The second part of the Winkler test: reduces acidifies the solution with H_2SO_4 in presence of KI. The $Mn(SO_4)_2$ formed by the acid converts the iodide ions into iodine,

$Mn(SO_4)_2 + 2\ I^{-}(aq) \rightarrow \quad Mn^{2+}(aq) + I_2(aq) + 2\ SO_4^{2-}(aq)$

Thiosulfate solution is used, with a starch indicator, to titrate the iodine.

$2\ S_2O_3^{2-}(aq) + I_2 \rightarrow S_4O_6^{2-}(aq) + 2\ I^{-}(aq)$

5-Chlorine in water (residual chlorine)

Chlorine is used to destroy or deactivate a variety of unwanted chemicals and microorganisms in water and wastewater.
An uncontrolled excess of chlorine in water, whether free available or combined, can adversely affect the subsequent use of the water.

The following method is used for determination of Chlorine:

1- Iodometric method:

To the acidified water sample, add KI solution. The liberated iodine is titrated with $Na_2S_2O_3$ using starch solution as indicator . The reaction is carried out at pH 3 to 4.

6-Hydrogen sulphide (H_2S) in water:

Hydrogen sulphide occurs in water supplies as result of bacterial and /or chemical process
1- Titrimetric method :
To determine sulphide in water the sample is acidified with HCl. Then add excess standard iodine solution and titrate the excess iodine with standard thiosulphate

2-Colorimetric method:

Sulfide reacts with dimethyl-p-phenylenediamine (p-aminodimethyl aniline) in the presence of ferric chloride to produce methylene blue, a dye which is measured at a wavelength maximum of 625 nm.

7-Hardness of water:

Waters are usually class as hard or soft water according to their action in soap.

When hardness is reduced by boiling the portion which is temporary hardness is due to the bicarbonate of calcium and magnesium. The hardness remaining is permanent hardness is usually due to the presence of sulphate, chloride and nitrate of calcium and magnesium.

Methods for determination:

EDTA method:

The total calcium and magnesium content of the water sample can be determined by adjusting the pH of the sample to pH= 10 by using NH_4Cl/NH_4OH buffer , then titrated with standard EDTA using eriochrome black (EBT) as indicator.

To determine calcium hardness alone use buffer pH 12 and murexide as indicator. And the magnesium hardness is obtained by difference

8-Chloride in water:

Chloride in the form of Cl^- ion , is one of the major anion in the water Chloride is found naturally in groundwater through the weathering and leaching of sedimentary rocks and soils and the dissolution of salt deposits. Chloride is often attached to sodium, in the form of sodium chloride (NaCl), which is used extensively for snow and ice removal.
Chloride determined in potable water by three methods

1- Mohr method:

The Mohr method uses chromate ions as an indicator in the titration of chloride ions with a silver nitrate standard solution. After all the chloride has been precipitated as white silver chloride, the first excess of titrant results in the formation of a silver chromate precipitate, which signals the end point (1). The reactions are:

$Ag+ + Cl^- \longrightarrow AgCl_{(s)}$

$2Ag+ + CrO^{2-} \longrightarrow Ag_2 CrO_4 (s)$

2- Volhard method:

Volhard titration is an indirect (back titration) technique which is used if reaction is too slow or if there is no appropriate indicator selected for determining the equivalent point

Titration principle :

Silver solution is added Cl^-

$Cl^- + Ag+ \longrightarrow AgCl$ (precipitate)

excess

After reaction has completed, the precipitate is filtered, then the filtrate is titrated with a standardized thiocyanate solution.

$Ag+ + SCN^- \longrightarrow AgSCN$ (solution)

3- Mercurimetric method:

$Hg^{2+} + 2\ Cl^- \longrightarrow HgCl_2$

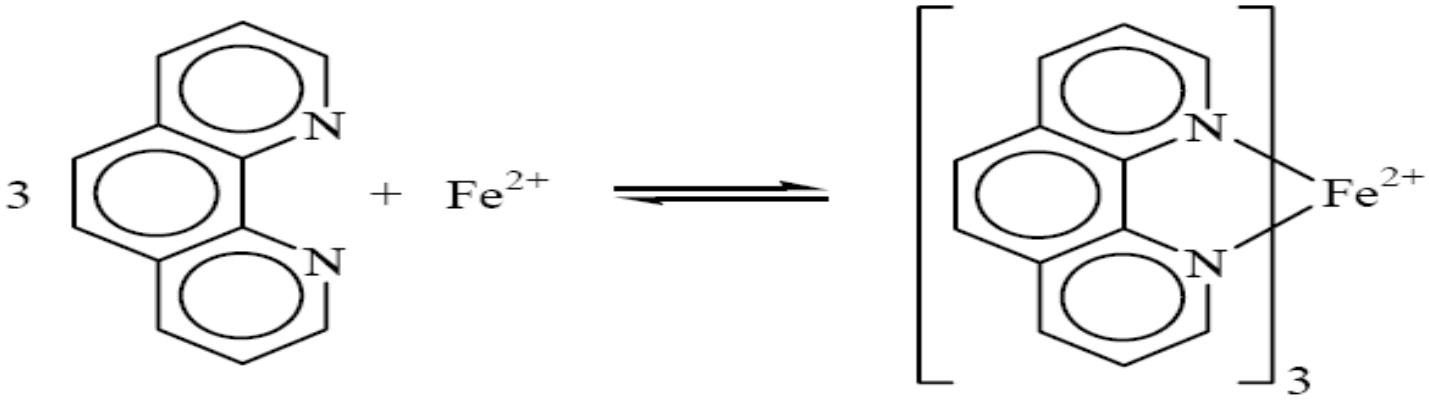
When halide ions is titrated with mercuric nitrate solution,$[Hg^{2+}]$ is not found at the equivalent point caused of precipitation of HgCl2 during the titration process.After equivalent point, $[Hg^{2+}]$ increases, react with indicator to form a Hg-indicator complex, e.g. Nitropruside form white precipitate, acid solution of diphenylcarbazide or diphenylcarbazon in forms intensive violet colour solution.

9-Iron in water:

Iron is one of the most common elements on earth, comprising approximately 5 percent of the earth's crust, thus it is hardly surprising that iron would be found in water, since water comes from ground sources. Iron is not normally a harmful substance, but its presence in water, due to the ground and other causes, can produce unpleasant effects, such as a bad taste, color or odor.

Method for determination:

Spectrophotometric method with Phenathroline method



o-Phenanthroline
FM 180.21

λ_{max} = 510 nm
Red complex

10- The Alkalinity and Acidity of water:

The alkalinity in water is due to presence of bicarbonate, carbonate, hydroxide and less frequently due to borate, silicate and phosphate.
The alkalinity is determined by the concentration of base, which measured by titration with strong acid in presence of indicator such as ph.ph or M.O.

The acidity of water is usually caused by the presence carbon dioxide, mineral acids and salts of strong acid and weak base.

The acidity determined by titrating the water sample by standard alkali using Ph.ph or M.O

11- Sulphate (SO_4^{--})

Sulphate ions usually occur in natural waters. Many sulphate compounds are readily soluble in water.

Method for determination:

Turbidimetric method:

This method is used for the determination of sulphate ions. Sulphate ion (SO_4^{--}) is precipitated in an acetic acid medium with Barium chloride ($BaCl_2$) , so as to form Barium sulphate ($BaSO_4$) crystals of uniform size. The reaction involved is given below:

$Ba^{++} + SO_4^{--} \longrightarrow BaSO_4$ (White suspension)

Light absorbance of the $BaSO_4$ suspension is measured by a photometer or the scattering of light by Nephelometer.

12- Sodium:

Sodium ranks sixth among the elements in order of abundance and is present in most natural water. The levels may vary from less than 1 mg Na/L to more than 500 mg Na/L. Relatively high concentrations may be found in hard water softened by the sodium exchange process. The ratio of sodium to total cations is important in agriculture and human pathology. Soil permeability can be harmed by a high sodium ratio.

also persons afflicted with certain diseases require water with low sodium concentration

Methods for analysis:
A. Inductively coupled plasma method
B. Flame Emission Photometric method

13- Potassium

Potassium ranks seventh among the elements in order of abundance, its concentration in most drinking water seldom reaches 100mg/L. Potassium is an essential element in both plant and human nutrition and occurs in groundwater as a result of mineral dissolution.

Methods for analysis

A. Inductively coupled plasma method
B. Flame Emission Photometric method

14- Fluoride (F^-)

Fluoride ions have dual significant in water supplies. High concentration of F^- causes dental fluorosis (disfiguerment of the teeth). At the same time, a concentration less than 0.8 mg/L results in 'dental caries'. Hence, it is essential to maintain the F^- concentration between 0.8 to 1.0mg/L in drinking water

Fluoride in water is determined calorimetrically. The method is based upon the reaction between the fluoride and red zirconium- alizarine lake. The fluoride forms a colorless, complex anion ZrF- and liberates free alizarin sulphonic acid which is yellow in acid solution.

Zr_alizarin lake + 6F→ alizarin + ZrF_6^{--}
(reddish color) (yellow)

Purification of water:

Water purification is the process of removing undesirable chemicals, biological contaminants, suspended solids and gases from contaminated water.

All natural water requires treatment for one or more of the following reasons:
1- To removal of color , odor, suspended matter ,organic matter and bacteria.
2- To remove metals ,e.g iron and manganese.
3- To remove dissolved solids e.g Ca and Mg
4- To neutralize acidity and correct corrosive activity.
The objects of all treatment are to obtain a clear and bright, colorless water , not too hard and without corrosive and solvent action on metals.

1-Physical water purification

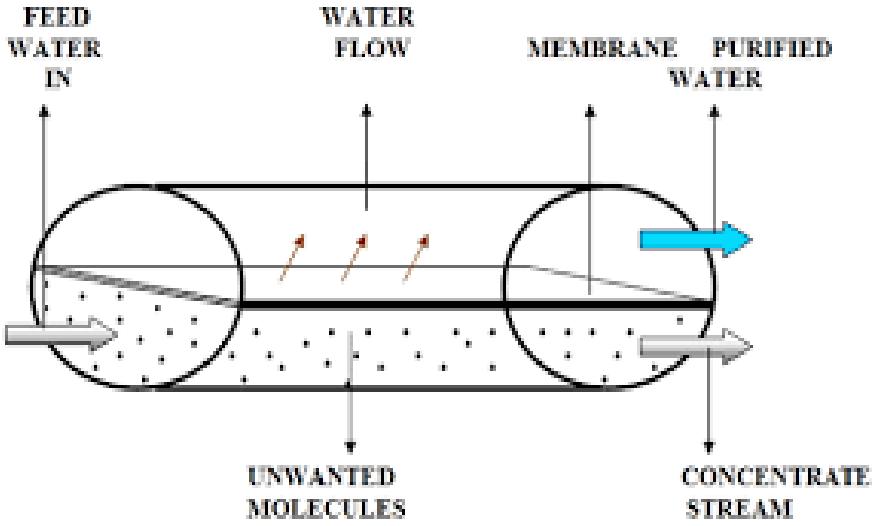
Physical water purification is primarily concerned with filtration techniques. Filtration is a purification instrument to remove solids from liquids. There are several different filtration techniques.

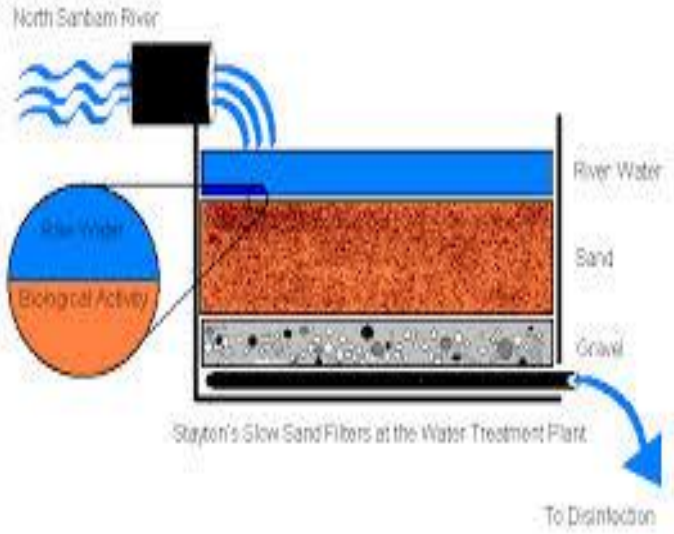
Sand filtration:

Sand filtration is a frequently used, very robust method to remove suspended solids from water. The filter medium consists of a multiple layer of sand with a variety in size and specific gravity. When water flows through the filter, the suspended solids precipitate in the sand layers as residue and the water, which is reduced in suspended solids, flows out of the filter.

Cross flow filtration:

Cross flow membrane filtration removes both salts and dissolved organic matter, using a permeable membrane that only permeates the contaminants. There are several different membrane filtration techniques, these are: micro filtration, ultra filtration, nano filtration and Reversed Osmosis (RO). Which one of these techniques is implemented depends upon the kind of compounds that needs to be removed and their particle size.


FEED WATER IN
WATER FLOW
MEMBRANE
PURIFIED WATER
UNWANTED MOLECULES
CONCENTRATE STREAM


North Saribam River
River Water
Sand
Gravel
Biological Activity
Slayton's Slow Sand Filters at the Water Treatment Plant
To Disinfection

2 -Chemical water purification

Chemical water purification is concerned with a lot of different methods. Which methods are applied depends on the kind of contamination in the water. Below, many of these chemical purification techniques are summed up.

Chemical addition

There are various situations in which chemicals are added, for instance to prevent the formation of certain reaction products. Below, a few of these additions are summed up:

- **Chelating agents** are often added to water, in order to prevent negative effects of hardness, caused by the deposition of calcium and magnesium.
- **Oxidizing agents** are added to act as a biocide, or to neutralize reducing agents.
- Reducing agents are added to neutralize oxidizing agents, such as ozone and chlorine.

Clarification:

Clarification is a multi-step process to remove suspended solids. First, coagulants are added. Coagulants reduce the charges of ions, so that they will accumulate into larger particles called flocs. The flocs then settle by gravity in settling tanks or are removed as the water flows through a gravity filter. Particles larger than 25 microns are effectively removed by clarification. Water that is treated through clarification may still contain some suspended solids and therefore needs further treatment.

Deionization and softening:

Deionization is commonly processed through ion exchange. Ion exchange systems consist of a tank with small beds of synthetic resin, which is treated to selectively absorb certain cations or anions and replace them by counter-ions. One of the most commonly used ion exchangers is a water softener. This device removes calcium and magnesium ions from hard water, by replacing them with other positively charged ions, such as sodium.

Disinfection:

Disinfection is one of the most important steps in the purification of water from cities and communities. It serves the purpose of killing the present undesired microorganisms in the water; therefore disinfectants are often referred to as biocides. There are a variety of techniques available to disinfect fluids and surfaces, such as: ozone disinfection, chlorine disinfection and UV disinfection.

Distillation :
Distillation is the collection of water vapor, after boiling the wastewater. With a properly designed system removal of organic and inorganic contaminants and biological impurities can be obtained, because most contaminants do not vaporize. Water will then pass to the condensate and the contaminants will remain in the evaporation unit.

pH-adjustment :
Municipal water is often pH-adjusted, in order to prevent corrosion from pipes and to prevent dissolution of lead into water supplies. The pH is brought up or down through addition of hydogen chloride, in case of a basic liquid, or sodium hydroxide, in case of an acidic liquid. The pH will be converted to approximately 7 to 7.5, after addition of certain concentrations of these substances.