Water is the most abundant chemical component in the biosphere. It is important to all life on the earth including human life.

Source of water

The main sources of water are:

- 1. **Ground water:** is the water that has percolated (مترشح) downward from the ground surface through the soil pores. Water is normally withdrawn from these reservoirs by well.
- 2. Surface water: All water on the surface of the Earth including lakes, ponds, rivers, streams and rainfall water. It is important source of public water supplies because of high withdrawn rates. Surface water supplies are not reliable (موثرق) as groundwater sources because the surface water is restricted by various sources of pollution, such as industrial and municipal wastes. Direct use of rainfall water is limited but it is important water source in a few areas.
- 3. Sea water: it is a valuable in unlimited quantities. This can be converted into fresh water by a number of processes. Conversion cost is 2 to 5 times higher than these of treating fresh water. Desalination is term used for removal of dissolved salts from water.
- 4. **Reclaimed wastewater:** is the water that has been treated sufficiently for direct reuse in industry and agriculture and for limited municipal application.

Utilization of water

The most important utilizations are:

- 1. *Irrigation*: the amount of water required for irrigation purpose various with climate of region and the type of crops that are raised.
- 2. *Domestic water supply*: the requirements vary from season to season and from rural to urban areas.
- *3. Power generation*: cooling is principle water use in thermal power generation and more than 99% of water used is required for condenser cooling.
- 4. *Industrial water use*: industry is much dependent on adequate water supply. The enormous demand of industry for water is obvious such as H₂SO₄ production, oil refinery, milk products, etc.

Wastewater

Wastewater can be defined as any water that contains impurities or pollutants in the form of solid, liquid or gases or their combinations in such a concentration that is harmful if disposed into the environment.

Classification of wastewater

Wastewater can be classified by their origin as: domestic wastewater and industrial wastewater.

- 1. Domestic wastewater: that is collected and discharged from residential and commercial establishments.
- 2. *Industrial wastewater*: is formed at industrial plants where water is used for various processes and also for washing and rinsing of equipment.

Types of water pollutants and their effects

The main pollutants in water are:

- 1. Oxygen demanding wastes:
 - a- Dissolved oxygen, DO:

Dissolved oxygen is the amount of oxygen dissolved in water to sustain the plant and animal life in any aquatic system. Oxygen-demanding waste are substances that oxidize in the receiving body of water. As bacteria decompose these waste, they utilize oxygen dissolved in the water, which reduces the remaining amount of DO. As DO drops, fish and other aquatic life are threatened and, in the extreme case, killed. In addition, as dissolved oxygen level fall, undesirable odors, tastes, colors reduce the acceptability. The EPA recommends at least 8mg/L DO for coldwater, but 5 mg/L of warmwater.

There are several measures of oxygen demand commonly used.

- Biochemical oxygen demand, BOD:

BOD is the amount of oxygen required by microorganisms to degrade the wastes (organic material) biologically. It is the most widely known measurement for assessing the water pollution by a given organic waste.

- Chemical oxygen demand. COD:

COD is the amount of oxygen needed to oxidize the wastes (organic and inorganic material) chemically.

2. pathogens:

Pathogens are a disease causing agents. Water is a potential carrier of pathogenic microorganisms. These pathogens are carried into the water bodies by sewage and waste from farms and various industries. Examples of pathogens associated with water include bacteria, which are responsible for cholera, bacillary dysentery, typhoid ..etc., viruses, which are responsible for infections hepatitis.. , protozoa, which cause amebic dysentery, giardiasis. At present, the most suitable method of removing them at water treatment plants is with coagulation, flocculation, and filtration.

3. Refractory organic compounds:

These include pesticides, herbicides, phenols, synthetic organic chemical and detergents. These compounds in contrast to the organic waste are not biodegradable and may persist for a long periods.

4. Nutrients:

Nutrients are the chemical material required to growth of aquatic life, Such as nitrogen and phosphorus. Nitrogen and phosphorus enter the water bodies directly from the manufacture and use of fertilizers and from the processing of biological material such as food and textiles. Nutrient enrichment can lead to blooms of algae, which eventually die and decompose. Their decomposition removes oxygen from water, that are insufficient to sustain normal life forms. Algae and decaying organic matter add color, turbidity, odor, and objectionable tastes to water that difficult to remove. The process of nutrient enrichment, called eutrophication.

5. Heavy metals:

Heavy metals is often to used to refer to metals with specific gravity greater than about 4 or 5. Most metals are toxic, including Al, As, Be, bismuth (Bi), Cd, Cr, cobalt (Co), Cu, Fe, Pb, Mn, Hg, Ni, selenium (Se), tin (Sn), titanium (Ti), and zinc (Zn). In term of their environmental impacts the most important heavy metals are mercury (Hg), lead (Pb), cadmium (Cd), and arsenic (As). Metals differ from other toxic substances in that they are totally nondegradable, which mean they are indestructible in the environment. Most of these are toxic and are capable of killing living organisms in the water bodies.

6. sediments:

These include soil, sand, and mineral particles or pulverized coal ash. Their effects increasing turbidity and consequently of reducing the amount of sunlight available to water plants. 7. Radioactive substances:

The refining of uranium is the most important source of radioactive waste producing radium, bismuth, etc. Radioactive substances can enter human with food and water and accumulated in blood, liver (الكبد), muscular tissues (الانسجه العضليه) causing to serious of health problem to human.

8. Thermal pollution

Power plant and industry use large quantities of water for cooling purpose. This could results in increase or decrease in the temperature of the water bodies and causing in the change in the percentage of dissolved oxygen in the aquatic media and decreases in the saturation percentage.

9. Oils:

Oils are important commodity and virtual for every human activity now. Oil wastes enter rivers and other water bodies from several sources like industrial effluents, oil refineries, storage tank, automobile waste oil, and petrochemical plants. Oil insoluble in water so it floats and spread rapidly into a thin layer. The lighter low molecular-weight elements, which are most toxic to organism, evaporate at slow rate effects on life in the water.

Wastewater treatment

The objective of wastewater treatment is to reduce the concentration of pollutants in water to the level so that the treated water will meet the acceptable quality standards and will not adversely affect the environment.

The wastewater treatment processes are usually grouped as:

- 1. Primary treatment: this process removes identifiable suspended solids and floating matter. Primary treatment system is always physical process.
- 2. Secondary treatment: this is designed to remove the organic matter that is soluble or in the colloidal form. These processes are commonly biological in nature.
- 3. Tertiary treatment or advanced treatment: this treatment may involve physical, chemical or biological processes or their various combinations depending on the impurities to be removed. The advanced waste treatment processes are expensive, and are used only when water produced is required to be of high quality.

1. Primary treatment

Primary treatment is mainly a removal of solids through the following steps:

a. Pretreatment:

Wastewater is pretreated to remove large floating and suspended solids. It consists of:

- 1. Screening: Screens of various sizes and shapes are used depending on the nature of solids to be removed. Fixed bar screens are the most common types of screen used in domestic wastewater facilities.
- 2. Grit removal: After screening the wastewater enters the grit chamber for removal of inorganic grit consisting of sand and gravels without removing the organic material.

b. Flotation:

Dissolved air flotation (DAF) is the simplest devices for the removal of grease and oil (G&O), and fine suspended solids (SS) from wastewater. Their simple operating principle using micro fine bubbles of air generated in the DAF vessel combine with insoluble contaminants in the wastewater, lifting them to the surface. Mechanical scrapers remove the floating sludge layer and the purified wastewater discharges to sewer.



c. coagulation –flocculation :

The whole treatment process of coagulation – flocculation can be divided into two distinct procedures. The first one termed coagulation, is the process whereby destabilization of a given colloidal suspension or solution is taking place. It is achieved with the use of appropriate chemicals, usually aluminum or iron salts, the so-called coagulant agents. The second sub-process, termed flocculation, refers to the induction of destabilized particles in order to come together, to make contact and thereby, to form large agglomerates, which can be separated easier usually through gravity settling. Coagulation usually completes in a very short period of time (e.g. about 10 s), whereas flocculation occurs usually over a period of 20 to 45 min.



d. Sedimentation:

In this step, the settleable solids are removed by gravitational settling. Settling tank is used to settle as much of the solids matter as possible. The settling tank which follows pretreatment is known as a primary clarifier. The solids settle at the bottom of the tank as a raw sludge. This sludge is removed as underflow either by vacuum or by raking it to a discharge point at the bottom of the tank, while the clarified liquid escapes as overflow. Sedimentation tank may be rectangular or circular tank.







section



list of symbols

- L (m) length
- W (m) width
- H (m) depth
- Q (m³/h) flow rate
- $s_{\rm o}~(m/h)~$ surface loading
- T (hr) detention time
- q (l/s m) weir load

design guidelines

$$s_{0} = \frac{Q}{L \cdot W} = 0.2 \cdot 1 \text{ m/h}$$

$$T = \frac{L \cdot W \cdot H}{Q} = 1 \cdot 3 \text{ hr}$$

$$q = \frac{Q}{3.6 \cdot W} \le 2 \cdot 3 \text{ l/s m}$$

$$\frac{L}{W} = 3 \cdot 8, H \sim 1.5 \cdot 2 \text{ m}$$

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2. Secondary biological treatment:

The water leaving the primary treatment has lost the sold matter but still contains the organic matter. This organic matter still represents a high demand for oxygen, BOD. This demand for oxygen must be removed. The objective of secondary treatment is thus to remove BOD. The following systems used for secondary biological treatment:

a. Activated sludge system:

Wastewater after primary treatment enters an aeration tank where the organic is brought into intimate contact with the sludge from the secondary clarifier. This sludge is heavily laden with microorganisms which are in active state of growth. Air is introduced into the tank, either in the form of bubbles through diffuser or by surface aerators. The microorganisms utilized the oxygen in the air and convert the organic matter into stabilized compounds such as NO3, SO4, CO2, and synthesis new bacteria cells. The effluent from the aeration tank containing the flocculent microbial mass known as the sludge is separated in settling tank which called a secondary or final clarifier. In the settling tank the separated sludge exists without contact with organic and becomes activated. A portion of the activated sludge is recycled to the aeration tank as seed and the rest is wasted, as shown in Fig.16. The activated sludge system consists of:

1- Aeration tank. 2- Solid-liquid separator. 3- Recycle activated sludge.



Fig.15. Block diagram of the activated sludge system

b. Trickling-filter(biological-film system):

Wastewater is brought into contact with a mixed microbial population in the form of a slim film attach to the surface of a solid

support medium (rocks). Trickling filters are most popular for treating domestic sewage because of its case of operation.



Image 1: A schematic cross-section of the contact face of the bed media in a trickling filter^[5]



c. Sludge treatment and disposal:

Handling and disposal of sludge from secondary biological wastewater treatment plants is an important problem. The common unit operation of sludge treatment and disposal are concentration or thickening, digestion, conditioning, dewatering, oxidation, and safe disposal.

3. Tertiary treatment(Advanced treatment):

The effluent from a typical secondary treatment still contains a significant amount of various types of pollutants such as suspended solids, BOD, nutrient, dissolves solids, and toxic substances. A variety of methods are used to satisfy any of several specific goals which are:

- 1- Removal of suspended solids.
- 2- Removal of BOD.
- 3- Removal of nutrient.
- 4- Removal of dissolved solids

5- Chemical oxidation.

3.1. Removal of suspended solids (SS)

Several methods are used to remove of suspended solids, but the most commonly methods used are:

1-Microscreening 2- coagulation.

3.2. Removal of BOD

There are four main types

- 1- Aerobic ponds.
- 2- Facultative ponds.
- 3- Aerated ponds
- 4- Anaerobic ponds.

3.3. Removal of nutrient

Include removal of nitrogen and phosphorous as described below:

3.3.1. Nitrogen removal:

All forms of nitrogen in wastewater effluent are harmful. Two popular methods of nitrogen removal are:

3.3.1.1. Ammonia stripping:

After second treatment all the nitrogen exit as ammonia. This can be removed by stripping. The air stripping process can be simply defined as a unit process in which water and air are brought into contact with each other with the purpose of transferring volatile substances from water to air. The physico-chemical process of ammonia stripping consists in raising the wastewater pH to about 11, so the equilibrium during stripping will favourable for ammonia desorption in air. High temperatures (60 °C) improves the equilibrium conditions for the stripping which makes the treatment more compact (more kg of water can be treated per kg of air)

 $NH_4^+ + OH^- \leftrightarrow NH_4OH \leftrightarrow NH_3 \uparrow + H_2O$

3.3.1.2. Nitrification- denitrification:

Nitrification is the process in which bacteria convert ammonia nitrogen to nitrate ions(NO3-),. Increased nitrogen control utilizes aerobic bacteria to convert ammonia (NH4+) to nitrate (NO3-), which is nitrification, followed by an anaerobic stage in which different bacteria

convert nitrates to nitrogen gas (N2), which is denitrification. The overall process then is referred to as nitrification/denitrification.

The nitrification step actually occurs in two stage. Ammonia is converted to nitrite (NO2-)by Nitrosomonas, while Nitrobacter oxidize nitrites to nitrates. The combination of steps can be summarized by

$$NH_4^+ + 2O_2 + bacteria \rightarrow NO_3^- + NO_3^- + 2H^+ + H_2O_3^-$$

De-nitrification is the process of reduction of the nitrate ions, produced from nitrification process, by anaerobic bacteria.

$$2NO_3^-$$
 + Organic matter + bacteria $\rightarrow N_2 \uparrow + CO_2 + H_2O$

Which release harmless, elemental nitrogen gas. The energy to drive this reaction comes from the organic matter. It is noted that only 30% is normally removed in a conventional secondary treatment facility.

3.3.2 Phosphorous removal:

The main processes used for the removal of phosphorous from wastewater are:

- 1- Chemical precipitation,
- 2- Biological phosphorous removal.

Chemical precipitation:

Only about 30% of the phosphorus in municipal wastewater is removed during conventional primary and biological treatment.

Phosphorus in wastewater exist in many forms, but all of it ends up as orthophosphate (H2PO4-, HPO4-2, and PO4-3). Removing phosphate is most often accomplished by adding a coagulant, usually alum [Al2(SO4)3] or lime [Ca(OH)2]. The pertinent reaction involving alum is:

$$Al_2(SO_4)_3 + 2PO_4^{-3} \rightarrow 2AlPO_4 \downarrow + 3SO_4^{-2}$$

3.3.3. Removal of dissolved solids.

The dissolved solids are both organic and inorganic types. Number methods have been used for the removal:

- 1- Adsorption by activated carbon.
- 2- Solvent extraction.
- 3- Ion exchange.
- 4- Reverse osmosis.

5- Electrodialysis.

3.3.3.1. Adsorption:

Adsorption can be defined as the accumulation of one substance on the surface of another. The substance undergoing accumulation, and thus being adsorbed, is called the adsorbate, and the substance on which the accumulation is taking place is called the adsorbent. The adsorbate can be dissolved, in which case it is called the solute, or it can be of the nature of suspended solids as in a colloidal suspension. Colloidal suspensions of liquids or gases can also be adsorbed.

Adsorption is divided into the two sub-categories of physical adsorption (physisorption) and chemical adsorption (chemisorption).

Physical Adsorption The process is an attraction between the adsorbate and adsorbent exists by the formation of intermolecular electrostatic, such as van der Waals forces, or may be dependent on the physical configuration of the adsorbent such as the porosity of activated carbons.

Chemical Adsorption involves the transfer of electrons between the adsorbent and the adsorbate with the formation of chemical bonds, by chemical reaction, between the two species causing adhesion of the adsorbate molecules.

The Adsorbent

Activated carbon is the most common adsorbent in use for industrial wastewater treatment. Other adsorbents include synthetic resins, activated alumina, silica gel, fly ash, and shredded tires,. Because adsorption is a surface phenomenon, a desirable characteristic of an adsorbent is a high surface-to-volume ratio. Surface-to-volume ratios are increased in two ways: by decreasing the size of particles of adsorbent and by creating a network of pores or "tunnels" within the particles of adsorbent.

Most adsorbents have weak negative charges on their surfaces; therefore, the pH of the wastewater being treated has an influence on the adsorptive process. This is because hydrogen ions repress the negative surface charges at lower pH values. Also, at low pH conditions, there is an increase in adsorption of dissolved or suspended substances that tend to have a negative surface.

3.3.3.2. Ion Exchange

Ion exchange is a physical treatment process in which ions dissolved in a liquid or gas interchange with ions on a solid medium. The ions on the solid medium are associated with functional groups that are attached to the solid medium, which is immersed in the liquid or gas. Typically, ions in dilute concentrations replace ions of like charge and lower valence state; however, ions in high concentration replace all other ions of like charge. For instance, calcium ions or ferric ions in dilute concentrations in water or wastewater replace hydrogen or sodium ions on the ion exchange medium.

The ion exchange material can be solid or liquid, and the bulk solution can be a liquid or a gas.

Naturally occurring materials that have ion exchange capability include soils, lignin, humus, wool, and cellulose. The ion exchange capacity of soils is made use of by land treatment systems. Synthetic ion exchange resins of high capacity are manufactured.

TYPES OF RESINS

1- Strongly Acidic Cation Resins

Strongly acidic cation resins derive their exchange activity from sulfonic functional groups (HSO). The major cations in water are calcium, magnesium, sodium, and potassium and they are exchanged for hydrogen in the strong acid cation exchanger when operated in the hydrogen cycle.

It shows the cations (H+) in combination with the major anions, the bicarbonate, sulfate, and chloride anions:

Ca $2HCO_2$ Mg $.SO_4 + 2RSO_3H + \leftrightarrow 2RSO_3 Mg + H_2SO_4$ Na 2C1Na 2HC1

Note : *that R represents the complex resin matrix.*

Because these equilibrium reactions are reversible, when the resin capacity has been exhausted it can be recovered through regeneration with a mineral acid.

2- Weakly Acidic Cation-exchange Resins

Weakly acidic cation exchange resins have carboxylic groups (COOH) as the exchange sites. Weakly acidic resins are used primarily for softening and dealkalization, frequently in conjunction with a strongly acidic polishing resin. These reactions are also reversible and permit acid regeneration to return the exhausted resin to the hydrogen form. It can be regenerated with the waste acid from a strong-acid cation exchanger.

3- Strongly basic anion-exchange resins

Strongly basic anion-exchange resins derive their functionality from the quaternary ammonium exchange sites (methyl and ethanol groups). In the hydroxide form, the strongly basic anion will remove all the commonly encountered inorganic acids according to these reactions:

H ₂ SO4 2HC1				SO ₄ 2Cl
H ₂ SiO ₃ }	+	2ZOH	\leftrightarrow	2 HSi 0_3 + H ₂ O
H_2CO_3				HCO ₃

Like the cation resin reactions, the anion-exchange reactions are also reversible and regeneration with a strong alkali, such as caustic soda, will return the resin to the hydroxide form.

3- Weakly Basic Anion Resins.

Weakly basic anion resins derive their functionality from primary (R-NH), secondary (R-NHR'), tertiary (R-N-R'2), and sometimes quaternary amine groups. The weakly basic resin readily absorbs such free mineral acids as hydrochloric and sulfuric, and the reactions may be represented according to the following:

$$H_2SO_4 + 2ZOH \iff 2ZSO_4 + 2HO$$

2HC1 2C1

Because the preceding reactions are also reversible, the weakly basic resins can be regenerated by applying caustic soda, soda ash, or ammonia.

3.3.4 Chemical oxidation

Chemical oxidation are widely used for disinfection, removing organic materials that are resistant to biological or other treatment processes and conversion of cyanides to innocuous products. This process can be done by:

- 1- Chlorine.
- 2- Ozone.

Filtration By Membrane technology.

Membrane filtration is a separation process in which a membrane acts as a physical and selective barrier between two phases. In the water treatment field, membrane is a finely porous medium allowing water to pass through the pores while retaining water constituents (Fig. 2.7). The effectiveness of the separation process strongly depends on the membrane characteristics, e.g., pore size, porosity and membrane material.



Fig. 2.7 Filtration classification - overview of membrane separation processes and associated components removal.

The transport through the membrane can occur when a driving force is present, e.g., a gradient based on temperature, electric potential, concentration or hydraulic pressure. In water treatment, pressure driven membrane processes are usually applied and transmembrane pressure (TMP) is a driving force for permeation.

Membrane configurations.

Depending on the manufacturing process, six basic configurations are distinguished: flat sheet (FS), hollow fibre (HF), multi tubular (MT), spiral wound, pleated filter cartridge and capillary tube. The first three membrane configurations are predominant in the municipal MBR market.



Fig. 2.8 Images of (a) flat sheet, (b) hollow fibre and (c) multi tube membranes, modules and trains.

MBR technology.

A membrane bioreactor (MBR) combines the activated sludge process with a membrane separation process. The reactor is operated as that of a conventional activated sludge process but without the need for secondary clarification and tertiary steps like sand filtration. Lowpressure membrane filtration, either MF or UF, is used to separate effluent from activated sludge.

MBR is a technology that will influence the future of wastewater treatment. MBR improves the quality of the effluent by providing enhanced organic matter and nutrient removal, greatly reduces the quantity of solids discharged and remove pathogens, what eliminates the need for disinfection. All these advantages come with a smaller plant footprint, saving land costs.

MBR configurations.

Depending on the location of the membranes, MBRs may be configured as side-stream MBRs (Figure 2.9a) or submerged, also called immersed, MBRs (Figure 2.9b).



Fig. 2.9 Process configurations of a membrane bioreactor: (a) side-stream and (b) submerged

The first MBRs were originally based on the cross-flow process and designed as sMBRs. In this system, the activated sludge is recirculated through the externally located membranes in a loop. Tubular membranes are commonly installed in the sMBRs.

The MBRs with submerged membranes are typically equipped with hollow fibre or flat sheet membranes. The membranes may be submerged in a separate membrane tank or placed directly in the bioreactor. The membrane surface is typically scoured by coarse bubble aeration providing a high shear force and reducing membrane fouling.

Oxygen demanding waste

Dissolved oxygen (DO)

Dissolved oxygen (DO) is essential for sustaining the plant and animal life in any aquatic system. There are four processes which actually affected the DO content:

- Reaeration
- Photosynthesis (تركيب ضوئي)
- Respiration (تنفس)
- Oxidation

Reaeration

Is the process by which oxygen transfer takes place form atmosphere to water.

The solubility of oxygen in fresh water at saturation point decreases with an increase in temperature, see Fig.16.



Fig.16. Saturation concentration of dissolved oxygen in fresh water

The rate of oxygen transfer (or rate of reaeration) depend on:

- 1- The rate of absorption through the air-water interface.
- 2- The rate of dispersion within the body of water near the surface.

The driving force for oxygen transfer is the difference between the saturation concentration C_S of dissolved oxygen and the actual concentration C_L present in water.

Since the solubility of oxygen in water is very low, the main resistance to mass transfer is on the liquid side of the interface so that the absorption is liquid-film controlled. The rate of oxygen transfer across unit area of surface in unit time, N, so that

$$N = k_L (C_S - C_L) \tag{16}$$

where

$$\begin{split} N &= Oxygen \ transfer \ rate, \ kg/m^2.s \\ C_s &= Saturation \ concentration \ of \ dissolved \ oxygen \ in \ water, \ mg/l \\ C_L &= Actual \ concentration \ of \ dissolved \ oxygen \ in \ water, \ mg/l \\ k_L &= Liquid \ phase \ mass \ transfer \ coefficient, \ m/s \ or \ m/day \end{split}$$

If the oxygen is transferred into a volume of water, V, having a total interfacial area, A, in contact with the gas phase, then the rate of oxygen transfer per unit volume of water is given by

$$\frac{dC_L}{dt} = \frac{NA}{V} = K_L \frac{A}{V} (C_s - C_L) = r(C_s - C_L)$$
(17)

where

$$\frac{dC_L}{dt}$$
 = is the oxygen transfer rate

 $K_L \frac{A}{V}$ = reaeration or reoxygenation rate constant, 1/day

 $(C_s - C_L)$ = is the deference between the saturation concentration of DO and the actual concentration of DO presented in water. This deference is often referred as the oxygen deficit, D:

$$D = \left(C_S - C_L\right) \tag{18}$$

Photosynthesis

Photosynthesis requires solar energy radiation. During the process, the green plants such as algae (الطحالب) utilize carbon dioxide and the inorganic nutrient in the water to synthesis organic materials and liberate oxygen.

Since the process occurs only during the present of sun-light, the DO level in the water increases during the day.

Respiration

At night the algae and the micro-organisms compete with each other for both dissolved oxygen and organic compounds. This bacterial respiration is responsible for the production of carbon dioxide and subsequent depletion of dissolved oxygen.



Fig.17 Diurnal variation of dissolved oxygen

Combination of the three effects of respiration, photosynthesis and reaeration results in a diurnal variation in dissolved oxygen concentration from the values that far exceed saturation during the day to much lower values or depletion at night.

Oxidation

In this process the oxygen is depleted by micro-organism during the oxidation of organic material

Pollution results when the oxygen demand exceeds the available oxygen

Biochemical Oxygen Demand, BOD

BOD is the measure of the oxygen utilized by micro-organism during the oxidation of organic material. BOD is the measurement for the water pollution.

If a given amount of organic matter is introduced, the rate of oxidation of organic matter (the rate of decline of BOD) can be approximated as a first-order chemical reaction whose may be expressed as:

$$\frac{dL}{dt} = -k_1 L \tag{19}$$

where

L = the BOD remaining in time t, mg/l

Integration of Eq,19 at time t = 0 and $L = L_u$:

$$\int_{L}^{L_{u}} \frac{dL}{L} = k_1 \int_{t}^{0} dt$$

To get

$$\frac{L}{L_{u}} = \exp\left(-k_{1}t\right) = 10^{-k_{1}'t}$$
(20)

$$k_1' = \frac{\kappa_1}{2.303}$$

where

 L_u = the ultimate BOD, mg/l k_1 = the deoxygenation constant, 1/day.

The ultimate BOD means the original concentration of the organic material before any biological action has occurred.

The amount of BOD remaining at any time t, equals

.

$$L = Lu\left(10^{-k_1't}\right) \tag{21}$$

If Y represent the amount of BOD utilized at any time t, then

$$L_{u} = L + Y \tag{22}$$

or

$$Y = L_u - L = L_u \left(1 - 10^{-k_1' t} \right)$$
(23)

A standard way to measure the BOD is to determine the amount of oxygen required by bacteria during the first five days of decomposition at $20^{\circ}C$:

$$Y_5 = L_u - L_5 = L_u \left(1 - 10^{-5k_1^{/}} \right)$$
(24)

$$Y_5 = \text{the 5-day BOD at 20°C}$$

The relationship among L, L_u and Y is shown in Fig.s 18 and 19. Fig.18 shows the BOD remaining versus time.



Fig.18 BOD remaining versus time

Fig.19 shows the BOD utilized versus time:



Several methods are a available for determining k_1^{\prime} and L_u which include:

(1) The least square methods. (2) The method of moments. (3) The daily difference method. (4) The rapid rate method. (5) The Thomas method.

The Thomas method is probably the simplest to use. This method is based on the similarity of two functions:

$$\left(1 - 10^{-k_1't}\right)$$

$$2.3k_1't \left[1 + (2.3/6)k_1't\right]^{-3}$$
(25)

Using this method the following equation can be written as:

$$\left(\frac{t}{Y}\right)^{\frac{1}{3}} = \left(2.3k_1^{\frac{1}{2}}L_u\right)^{\frac{1}{3}} + \left[\frac{\left(k_1^{\frac{1}{2}}\right)^{\frac{2}{3}}}{3.43\left(L_u\right)^{\frac{1}{3}}}\right]t$$
(26)

A plot of $(t/Y)^{\frac{1}{3}}$ versus time t will give a straight line whose slope, b and intercept a can be used to calculate $k_1^{\frac{1}{3}}$ and L_u

$$k_1^{\prime} = 2.61 \frac{b}{a} \tag{27}$$

$$L_{u} = \frac{1}{2.3k_{1}^{\prime}a^{3}}$$
(28)

Table.2 show some typical values of k_1^{\prime} and L_u .

Table.2. Some typical v	values of	k_1^{\prime}	and L_{u}
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Type of waste	ewater	k_1^{\prime} (day ⁻¹)	L _u (mg/l)	
Weak wastewater		0.152	150	
Strong wastewater		0.165	200	
Primary	sewage	0.152	75-150	
effluent Secondary	sewage	0.052-0.100	15-75	



Fig.20. BOD utilized versus time

The reaction rate constant k_1^{\prime} depends on the temperature (T) and may be described by Van't Hoff Arrhenius equation:

(29)

$$\frac{d\left(\ln k_{1}^{\prime}\right)}{dT} = \frac{E}{R_{u}T^{2}}$$

where

 $E = activation energy, cal/mol R_u = universal gas constant T reaction temperature, K$

Integration between the limiots of T_o and T we get:

$$\ln \frac{k_{1,T}^{\prime}}{k_{1,T_{o}}^{\prime}} = \frac{E(T-T_{o})}{R_{u}TT_{o}}$$

(30)

For most cases of the wastewater treatment processes the term E/R_uTT_o is nearly constant, then Eq.30 becomes:

$$\ln \frac{k_{1,T}^{\prime}}{k_{1,T_{o}}^{\prime}} = const.(T - T_{o})$$

Therefore

$$\frac{k_{1,T}^{\prime}}{k_{1,T_o}^{\prime}} = \exp\left[const\left(T - T_o\right)\right]$$

Let $exp(const) = \theta$ = temperature coefficient, then Eq.32 becomes:

(33)
$$k_{1,T}' = k_{1,T_o}' \theta^{(T-T_o)}$$

Oxygen sag curves

The discharge of waste into a body of water results in the depletion of dissolved oxygen level (deoxygenation) as the wastes oxidized by bacteria. Opposite to this drop in dissolved oxygen (depletion) is reaeration which replace oxygen through the surface of water, at a rate which is proportional to the rate of depletion of oxygen below the saturation value.

The simulations action of de-oxygenation and re-aeration produces a typical pattern in the dissolved oxygen concentration of aquatic system. This pattern is known as the dissolved-oxygen sag and the typical curve is shown in the figure below.



Distance downstream (or time)

Fig.21 Oxygen sag curve

The following conclusion can be seen from oxygen sag curve:

- 1. Initially the sag curve drops as the waste deplete the oxygen faster than it can be replaced.
- 2. At the point where the dissolved oxygen (DO) is a minimum, the rate of reaeration becomes equal to the rate of deoxygenation. This point is the critical point.
- 3. Beyond the critical point, the rate of reaeration exceeds the rate of deoxygenation and dissolved oxygen levels (DO) begin to increase and eventually return to normal.

The simultaneous action of deoxygenation and reaeration can be described by the equation:

$$\frac{dD}{dt} = k_1 L - k_2 D \tag{28}$$

where

D = dissolved oxygen deficit, mg/l or kg/m³

= concentration of organic material (the BOD remaining in time t), L $mg/l \text{ or } kg/m^3$

 $k_1 = deoxygenation constant, day^{-1}$ $k_2 = reaeration constant, day^{-1}$

L can be expressed in terms of ultimate BOD, L_u as (see Eq.14):

$$L = L_u e^{-k_1 t} \tag{29}$$

Substituting Eq.29 in Eq.28 and integrating we gate:

$$D = \frac{k_1 L_u}{k_2 - k_1} (e^{-k_1} - e^{-k_2 t}) + D_o e^{-k_2 t}$$
(30)

where D is the dissolved oxygen deficit in time t, (mg/l) and D_o = initial oxygen deficit at the point of waste discharge (mg/l).

since

$$e^{-kt} = 10^{-k't}$$

where

$$k' = \frac{k}{2.303}$$

$$D = \frac{k_1' L_u}{k_2' - k_1'} (10^{k_1'} - 10^{k_2'})$$
(31)

then

Both k_1^{\prime} and k_2^{\prime} are temperature dependent. The temperature effects on k_1^{\prime} as in Eq.27. The temperature effect on k_2^{\prime} can be evaluated as follows:

$$k_{2,T}' = k_{2,20}' (1.047)^{T-20}$$
(32)

where

 $k'_{2,T}$ = re-aeration constant at temperature T °C $k'_{2,20}$ = re-aeration constant at temperature 20 °C

The critical dissolved oxygen deficit D_c , where the rate of oxygen utilized for waste material decomposition equals to the rate of atmosphere reaeration, and this can be evaluated by simply setting dD/dt = 0 in Eq.28 and $D = D_o$, as:

$$k_1 L - k_2 D_c = 0$$
$$L = L_u e^{-k_1 t}$$

and

then

(33a)
$$k_2 D_c = k_1 L = k_1 L_u \exp(-k_1 t_c)$$

 $D_c = \frac{k_1}{k_2} L_u \exp(-k_1 t_c)$ (33)

the critical time (t_c) can be obtained by differentiating Eq.30 with respect to t and setting dD/dt =0 to get:

$$t_{c} = \frac{1}{k_{2} - k_{1}} \ln \left[\frac{k_{2}}{k_{1}} \left(1 - D_{o} \frac{k_{2} - k_{1}}{k_{1} L_{u}} \right) \right]$$
(34)

 k_1^{\prime} can be evaluated from the BOD test in the laboratory

 k_2' must be determined from field information . O'Conner and Dobbins gave the following empirical equation for determining k_2' at 20 °C

$$k_2 = 3.9 \frac{V^{0.5}}{H^{1.5}} \tag{35}$$

where V = velocity of flow, m/s H = depth of flow, m The time required to reach the critical point is significant because at this point the conditions in the stream will be at their worst. The DO will be minimum and if it reaches zero, then anaerobic conditions may be prevail leading to the death of the aerobic aquatic inhabitants.