Advanced Waste Water Treatment

Removal of Dissolved Organic and Inorganic Substances by –

1. Precipitation,
2. Ion Exchange,
3. Reverse Osmosis,
4. Electro Dialysis,
5. Adsorption
6. Oxidation.

1. Precipitation

- Chemical precipitation is the most common method for removing dissolved metals from wastewater solution containing toxic metals.

- To convert the dissolved metals into solid particle form, a precipitation reagent is added to the mixture.

- A chemical reaction, triggered by the reagent, causes the dissolved metals to form solid particles

- Filtration can then be used to remove the particles from the mixture. How well the process works is dependent upon the kind of metal present, the concentration of the metal, and the kind of reagent used.

- In hydroxide precipitation, a commonly used chemical precipitation process, calcium or sodium hydroxide is used as the reagent to create solid metal hydroxides.

- However, it can be difficult to create hydroxides from dissolved metal particles in wastewater because many wastewater solutions contain mixed metals.

- Precipitation can be broadly divided into two categories:
- (1) chemical precipitation and
- (2) coprecipitation/adsorption.

- Chemical precipitation is a complex phenomenon resulting from the induction of supersaturation conditions

- Precipitation proceeds through three stages: (1) nucleation, (2) crystal growth, and (3) flocculation

Coprecipitation/Adsorption

- When a solid phase is precipitated from solution, impurities that are normally soluble under the conditions of the precipitation may adsorb onto nuclei or crystals and be removed with the parent solid as a single phase.

- This phenomenon is known as coprecipitation. Coprecipitation/adsorption is a co-removal process for removal of contaminants from wastewaters.

- **Also applied for the removal of heavy metals**.
- Chemical precipitation involves transforming a soluble compound into an insoluble form through the addition of chemicals

- Following are the advantages of precipitation/ coprecipitation contaminant removal processes:
- (1) low cost for high volume,
- (2) process is often improved by high ionic strength,
  (3) it is a reliable process well suited to osmotic control.

- Limitations include the following:

- (I) stoichiometric chemical addition requirements;
- (2) high-water-content sludge must be disposed of;
- (3) part per billion effluent contaminant levels may require two-stage precipitation;
- (4) processing is not readily applied to small, intermittent flows;
- (5) coprecipitation efficiency depends on initial contaminant concentration and surface area of the primary floc.

- Treatment of these wastewaters is usually accomplished through hydroxide precipitation; nearly 75% of the plating facilities employ precipitation treatment (primarily hydroxide treatment) as the treatment technique scheme for removal of heavy metals from solution.

- Chemical precipitation is the most common technique used for treatment of metal-containing wastewaters

2. Ion Exchange

- This technique has been used extensively to remove hardness, and iron and manganese salts in drinking water supplies.

- It has also been used selectively to remove specific impurities and to recover valuable trace metals like chromium, nickel, copper, lead and cadmium from industrial waste discharges.

- The process takes advantage of the ability of certain natural and synthetic materials to exchange one of their ions.

- A number of naturally occurring minerals have ion exchange properties.

- Among them the notable ones are aluminium silicate minerals, which are called zeolites.

- Synthetic zeolites have been prepared using solutions of sodium silicate and sodium aluminate.

- Alternatively synthetic ion-exchange resins composed of organic polymer with attached functional groups such as $–SO_3\ H^+$ (strongly acidic cation exchange resins), or $-\ COO^-H^+$ (weakly acidic cation exchange resins or $-N^+\ (CH_3)_3OH^-$ (strongly basic anion exchange resins) can be used.

- In the water softening process, the hardness producing elements such as calcium and magnesium are replaced by sodium ions.

- A cation exchange resin in sodium form is normally used. The water-softening capability of cation exchange can be seen when sodium ion in the resin is exchanged for calcium ion in solution.

$$2\,Res\,SO_3^-\,Na^+ + Ca^{2+} \rightarrow (Res\,SO_3^-)_2\,Ca^{2+} + 2Na^+ \quad \text{.............................}(2)$$

(where "Res" represents resin phase)

- The product water thus has high sodium content, which is not likely to be troublesome unless the original water is very hard.

- When the exchanger is saturated, it has to be regenerated to allow reuse of expensive resin.

- Regeneration can be achieved by sodium chloride solution which removes Ca2+ and Mg2+ ions from the resin.

- Since for regeneration large amounts of NaCl has to be used, appreciable amounts of sodium chloride can be introduced into sewage by this route.
- This problem can be overcome by using weakly acidic cation exchange resin such ResCOOH+ .
- These cation exchangers having -COOH as functional group are useful for removing alkalinity along with hardness.

- Alkalinity is generally manifested by bicarbonate ion. This ion is sufficiently basic to neutralise the acid of weak cation exchange.

- Another advantage with these resins is that these can be regenerated almost stoichiometrically with dilute strong acid, thus avoiding pollution problem caused by excess NaCl.

- This technique has also been successfully applied to the recovery of chromate from waste water in pigment manufacturing.

- The removal of inorganic solute is essential for complete water recycling.

- The effluent from secondary waste treatment contains 300-400 mg/L more dissolved inorganic material than does municipal water.

- The removal of these bulk inorganics can be efficiently done by reverse osmosis and electrodialysis .

3. Reverse Osmosis

- In the reverse osmosis process, demineralisation water is produced by forcing water through semipermeable membranes at high pressure.

- In ordinary osmosis, if a vessel is divided by a semipermeable membrane (one that is permeable to water but not the dissolved material), and one compartment is filled with water and other with concentrated salt solution, water diffused through the membrane towards the compartment containing salt solution until the difference in water levels on the two sides of the membrane creates a sufficient pressure to counteract the original water flow.

The difference in levels represents the osmotic pressure of the solution (fig.1a).

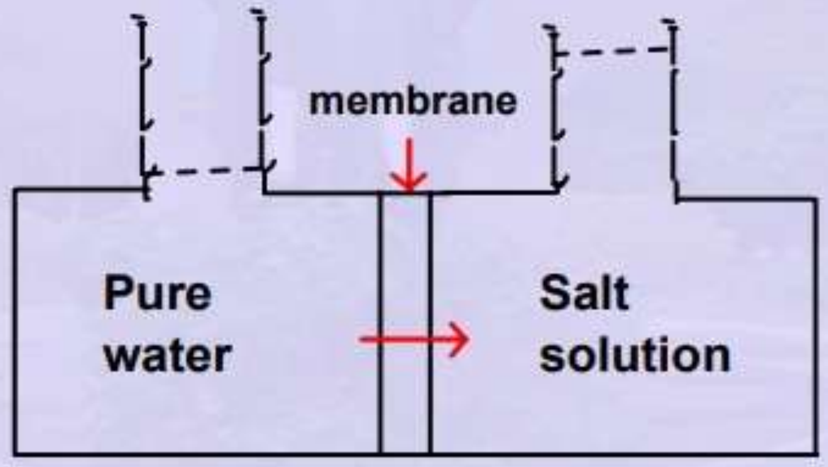


Fig 1a Osmosis

- The process can be reversed by applying sufficient pressure to the concentrated solution to overcome the osmotic pressure force the net flow of water through the membrane towards the dilute phase.

- The solute concentration (impurity) builds up on one side of the membrane while relatively pure water passes through the membrane .

- In order to obtain adequate solvent (water) flux through the membrane, pressures of the order of 4000 to 7000 kN/m2 (kilonewton/square metre) is required.

- Fig.1b represents the principle of operation of the reverse osmosis unit.

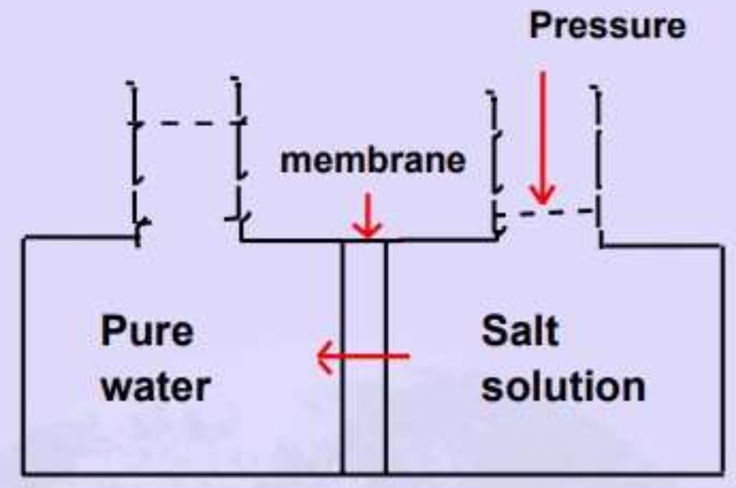
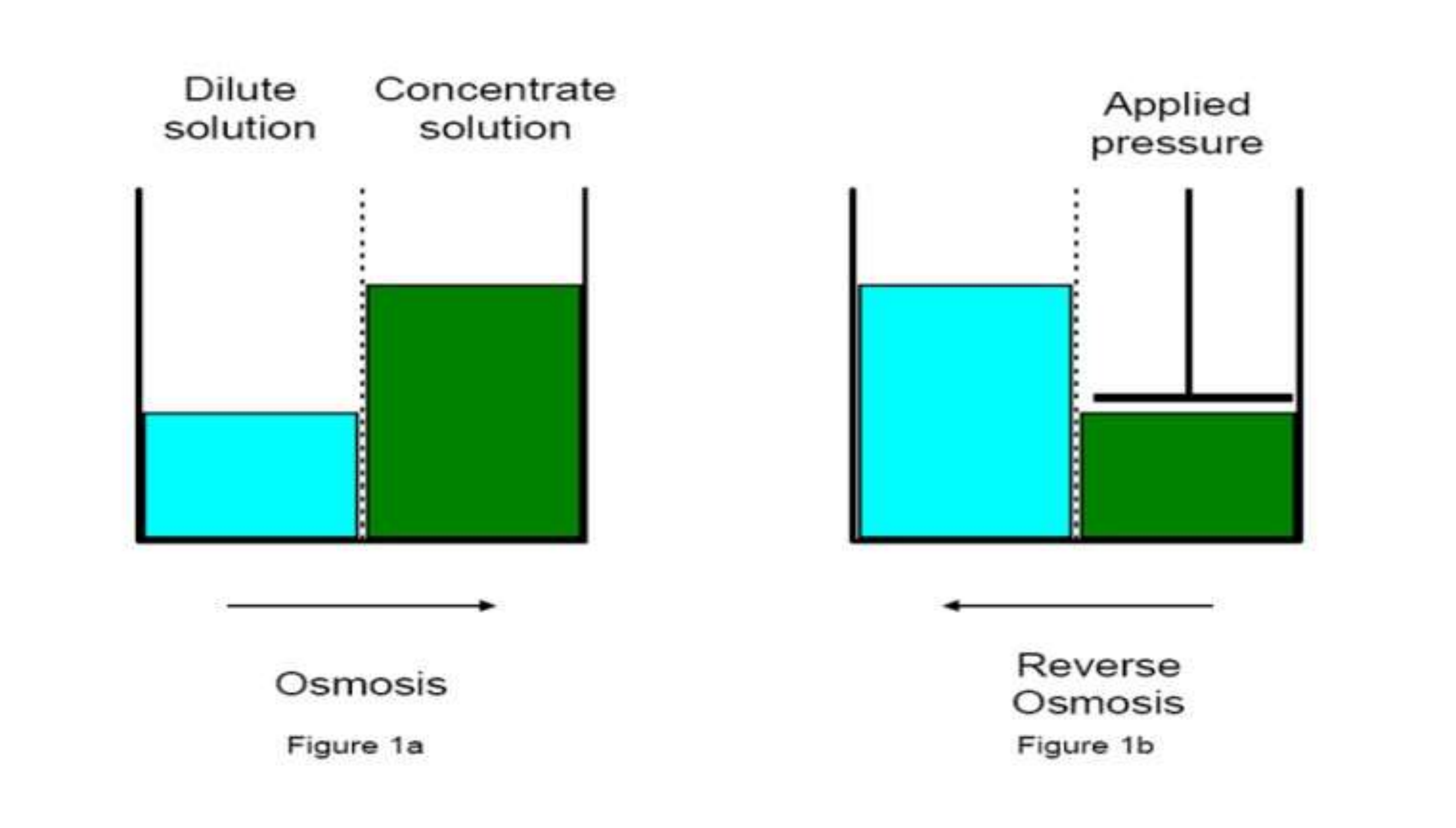


Fig 1b Reverse Osmosis


Dilute solution
Concentrate solution
Osmosis
Figure 1a
Applied pressure
Reverse Osmosis
Figure 1b

- Reverse osmosis is a membrane technology used for separation also referred as Hyperfiltration. In a typical RO system the solution is first filtered through a rough filter like sand or active carbon, or dual filter etc.

- If solution contains Ca++, Mg salts, iron, carbonates, then acid dosing system is introduced.

- The pH is adjusted and the solution is then filtered through micro cartridge filter (5-10 micron).

- The pretreated water is then pumped in to the RO tank with a high pressure pump.

- The membrane separates the pollutants in concentrated form in the reject stream and the pure water is collected as a permeate.

- Applications that have been reported for RO processes include the treatment of organic containing wastewater, wastewater from electroplating and metal finishing, pulp and paper, mining and petrochemical, textile, and food processing industries, radioactive wastewater, municipal wastewater, and contaminated groundwater

4. Electrodialysis

- Electrodialysis uses ion-selective membranes and an electrical potential difference to separate anions and cations in solution.

- Fig.2 shows a simple dialysis cell in which waste water is deionised. As shown in the figure two types of membranes (anionic and cationic) are arranged alternatively to form many compartments between the electrodes placed at the two ends.

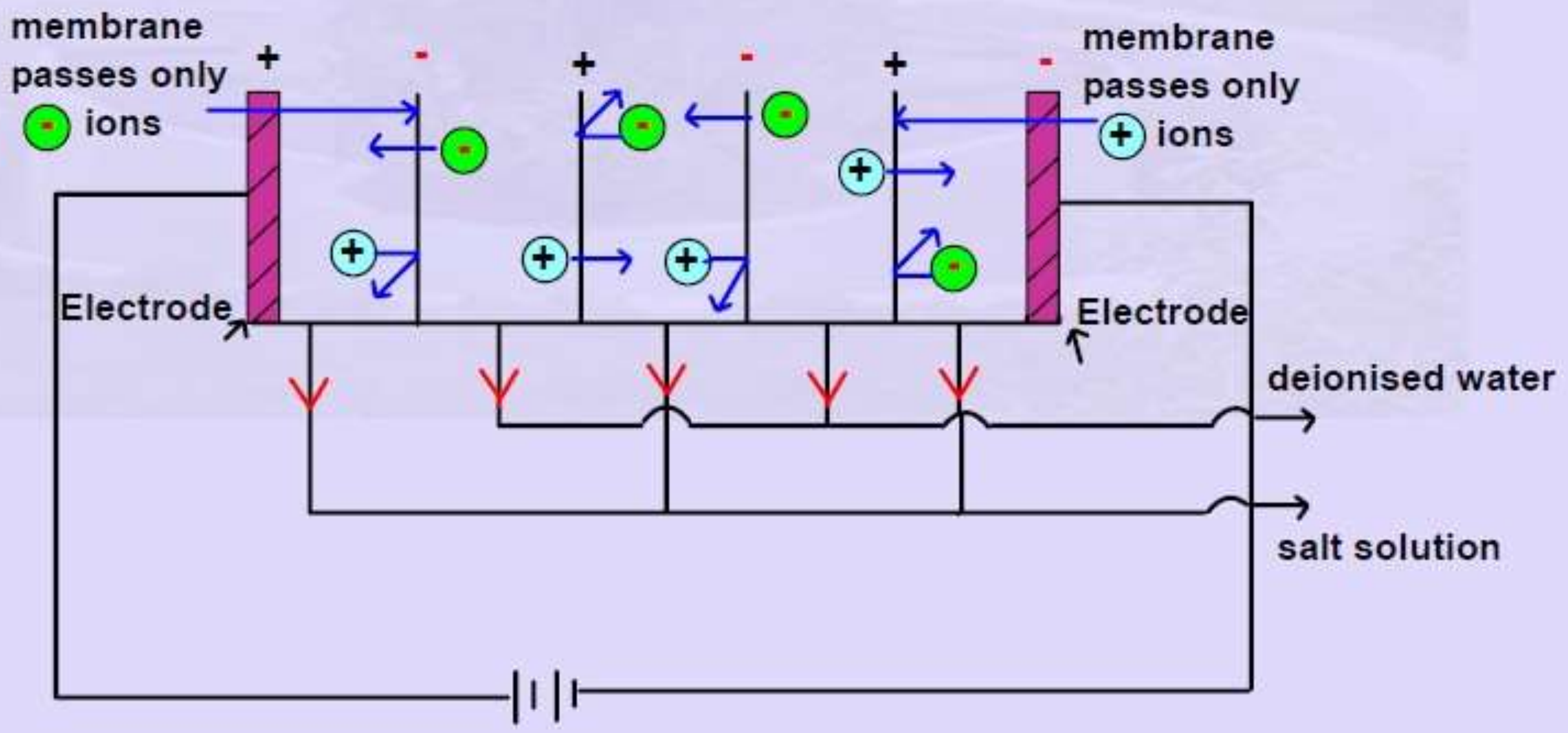


Fig.2 Electrodialysis cell

- When the voltage is applied across the cell containing mineralised water, the anions migrate to the positive electrode and the cations migrate to the negative electrode.

- This causes solution in alternate compartments to become more concentrated while that in the remaining becomes more dilute.

- The electric power requirement is proportional to the number of ions removed from the water.

- In the electrodialysis process, organic molecules are not removed and they can collect on and clog the membranes.
- Another disadvantage of this method is that it still leaves concentrated waste water to be disposed of by some appropriate scheme.
- The process does not require any chemical additives and has low energy requirements and as such it can be an economically feasible means of demineralisation.

4. Adsorption

- Removal of dissolved organic compounds

- One of the most commonly used techniques for removing organics involves the process of adsorption, which is the physical adhesion of chemicals on to the surface of the solid.

- The effectiveness of the adsorbent is directly related to the amount of surface area available to attract the particles of contaminant.

- The most commonly used adsorbent is a very porous matrix of granular activated carbon, which has an enormous surface area (~ 1000 m2/g).

- Adsorption on activated carbon is perhaps the most economical and technically attractive method available for removing soluble organics such as phenols, chlorinated hydrocarbons, surfactants, and colour and odour producing substances from waste water.

- Granular activated carbon treatment systems consist of a series of large vessels partially filled with adsorbent.

- Contaminated water enters the top of each vessel, trickles down through granulated activated carbon, and is released at the bottom.

- After a period of time, the carbon filter becomes clogged with adsorbed contaminants and must be either replaced or regenerated.

- Regeneration of the carbon is accomplished by heating it to 950^{o}C in a steam air atmosphere. This process oxidises surface, with an approximately 10% loss of carbon.

- Synthetic organic polymers such as Amberlite XAD-4 have hydrophobic surfaces and are quite useful in removing relatively insoluble organic compounds such as chlorinated pesticides.

- These absorbents are readily regenerated by solvents such as isopropanol and acetone.

5. Oxidation

- Advanced oxidation processes (abbreviation: AOPs), in a broad sense, are a set of chemical treatment procedures designed to remove organic (and sometimes inorganic) materials in water and wastewater by oxidation through reactions with hydroxyl radicals.

- More specifically refers to a subset of such chemical processes that employ ozone (O3), hydrogen peroxide (H2O2) and/or UV light. One such type of process is called in situ chemical oxidation.

- AOPs rely on in-situ production of highly reactive hydroxyl radicals (·OH).

- These reactive species are the strongest oxidants that can be applied in water and can virtually oxidize any compound present in the water matrix, often at a diffusion controlled reaction speed.

- Consequently, ·OH reacts unselectively once formed and contaminants will be quickly and efficiently fragmented and converted into small inorganic molecules.

- Hydroxyl radicals are produced with the help of one or more primary oxidants (e.g. ozone, hydrogen peroxide, oxygen) and/or energy sources (e.g. ultraviolet light) or catalysts (e.g. titanium dioxide).

- Precise, pre-programmed dosages, sequences and combinations of these reagents are applied in order to obtain a maximum •OH yield.

- In general, when applied in properly tuned conditions, AOPs can reduce the concentration of contaminants from several-hundreds ppm to less than 5 ppb and therefore significantly bring COD and TOC down, which earned it the credit of "water treatment processes of the 21st century"

- The AOP procedure is particularly useful for cleaning biologically toxic or non-degradable materials such as aromatics, pesticides, petroleum constituents, and volatile organic compounds in wastewater.

- Additionally, AOPs can be used to treat effluent of secondary treated wastewater which is then called tertiary treatment.

- The contaminant materials are converted to a large extent into stable inorganic compounds such as water, carbon dioxide and salts, i.e. they undergo mineralization.

- A goal of the wastewater purification by means of AOP procedures is the reduction of the chemical contaminants and the toxicity to such an extent that the cleaned wastewater may be reintroduced into receiving streams or, at least, into a conventional sewage treatment.

Removal of Heavy Metals

- Treatment processes for heavy metal removal from wastewater include precipitation, membrane filtration, ion exchange, adsorption, and Co-precipitation/ adsorption.

Removal of Nutrients

- Most of the organic matter present in waste water is decomposed during secondary treatment. These water contains plenty of nitrates, phosphates and ammonium salts, which are the products of biodegradation.

- Phosphates, nitrates and ammonium salts are essential plant nutrients. If released into natural waters, which results in eutrophication.

- In addition these water also contain large populations of bacteria, algae, fungi, protozoan etc.
- The microbial population present in these water has to be eliminated as many of these microbes are pathogens.
- After secondary treatment, next phase called tertiary treatment is carried out, which removes much of plant nutrients and microbes.

- This is done in biological ponds, in which waste water is allowed to stay for a period of time, which depends on the type of water.

- Biological ponds are a series of simple shallow tanks about 1m in depth which are interconnected with each other.

- Rich population of algae develop in these ponds as plant nutrients are absorbed. Primary producers (algae) supports a series of consumers.

- The mineral content of the water passes on to higher trophic levels and is eliminated.

- Profuse algal growth generates enough oxygen in the system to support a diverse community of aerobes which consume much of harmful pathogenic forms.

- After lagooning in biological ponds the waste water is subjected to the process of disinfection which further eliminates the pathogenic organisms still present.

- This may be achieved by chlorination, treatment with potassium permanganate, UV radiation etc. after the tertiary treatment the waste water is finally fit for being released in to a natural water body.

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Water pollution treatment using constructed wetlands

- A constructed wetland (CW) is an artificial wetland created for the purpose of treating municipal or industrial wastewater, greywater or stormwater runoff.

- It may also be created for land reclamation after mining, refineries, or other ecological disturbances such as required mitigation for natural areas lost to land development.

- Constructed wetlands are engineered systems that use natural functions of vegetation, soil, and organisms to treat different water streams.

- Depending on the type of wastewater that has to be treated the system has to be adjusted accordingly which means that pre- or post-treatments might be necessary.

- Constructed wetlands can be designed to emulate the features of natural wetlands, such as acting as a biofilter or removing sediments and pollutants such as heavy metals from the water.

- Some constructed wetlands may also serve as a habitat for native and migratory wildlife, although that is usually not their main purpose.

- The planted vegetation plays a role in contaminant removal but the filter bed, consisting usually of a combination of sand and gravel, has an equally important role to play.

Types

1. Free water surface constructed wetlands are efficient in removal of organics through microbial degradation and settling of colloidal particles.

- Suspended solids are effectively removed via settling and filtration through the dense vegetation.
- Nitrogen is removed primarily through nitrification (in water column) and subsequent denitrification (in the litter layer), and ammonia volatilization under higher pH values caused by algal photosynthesis.
- Phosphorus retention is usually low because of limited contact of water with soil particles which adsorb and/or precipitate phosphorus.

- Plant uptake represents only temporal storage because the nutrients are released to water after the plant decay.

- Constructed wetlands with FWS are frequently used in North America and Australia

2. Constructed Wetlands with Horizontal Subsurface Flow (HF CWs)

- Consist of gravel or rock beds sealed by an impermeable layer and planted with wetland vegetation.

- The wastewater is fed at the inlet and flows through the porous medium under the surface of the bed in a more or less horizontal path until it reaches the outlet zone, where it is collected and discharged.

- In the filtration beds, pollution is removed by microbial degradation and chemical and physical processes in a network of aerobic, anoxic, anaerobic zones with aerobic zones being restricted to the areas adjacent to roots where oxygen leaks to the substrate.

3. Constructed Wetlands with Vertical Subsurface Flow

- Vertical flow constructed wetlands (VF CWs) were originally introduced by Kathe Seidel to oxygenate anaerobic septic tank effluents.

- However, the VF CWs did not spread as quickly as HF CWs probably because of the higher operation and maintenance requirements due to the necessity to pump the wastewater intermittently on the wetland surface.

- The water is fed in large batches and then the water percolates down through the sand medium. The new batch is fed only after all the water percolates and the bed is free of water.

- This enables diffusion of oxygen from the air into the bed. As a result, VF CWs are far more aerobic than HF CWs and provide suitable conditions for nitrification.

- On the other hand, VF CWs do not provide any denitrification.

- VF CWs are also very effective in removing organics and suspended solids. Removal of phosphorus is low unless media with high sorption capacity are used.

Bioremediation

- Bioremediation is a waste management technique that involves the use of organisms to neutralize pollutants from a contaminated site.

- According to the United States EPA, bioremediation is a "treatment that uses naturally occurring organisms to break down hazardous substances into less toxic or non toxic substances".

- Technologies can be generally classified as *in situ* or *ex situ*.

- *In situ* bioremediation involves treating the contaminated material at the site, while *ex situ* involves the removal of the contaminated material to be treated elsewhere.

- Some examples of bioremediation related technologies are phytoremediation, bioventing, bioleaching, landfarming, bioreactor, composting, bioaugmentation, rhizofiltration, and biostimulation.

- It uses naturally occurring bacteria and fungi or plants to degrade or detoxify substances hazardous to human health and/or the environment.

- The microorganisms may be indigenous to a contaminated area or they may be isolated from elsewhere and brought to the contaminated site.

- Contaminant compounds are transformed by living organisms through reactions that take place as a part of their metabolic processes

- Biodegradation of a compound is often a result of the actions of multiple organisms.

- When microorganisms are imported to a contaminated site to enhance degradation we have a process known as bioaugmentation.

Biostimulation - The addition of organic or inorganic compounds to cause indigenous organisms to effect remediation of the environment, e.g. fertilizer, surfactants.

Bioaugmentation - The addition of organisms to effect remediation of the environment,
e.g. contaminant degrading bacteria injection into a contaminant zone

Traditional Water Purification Techniques.

- All over the world, rural communities have adopted simple and rudimentary treatment techniques that mainly aim at filtering out the visible impurities from the water collected from local sources.

- Though these traditional methods are expedient and can remove certain types of particles in water, they do not provide water necessarily of what would be considered, under the present day situation, as drinking quality.

- However, it can be considered that these methods provide water of quality that is acceptable to these rural communities, and in most of the cases, with a further simple step of disinfection, they could yield water free from pathogens.

- Some of the traditional treatment methods are:

1. Filtration through winnowing sieve (used widely in Mali).

2. Filtration through cloth (commonly used in villages in India, Mali and the southern part of Niger).

3. Filtration through clay vessels (used in Egypt).

4. Clarification and filtration through plant material (commonly used in Tamil Nadu and Kerala, India).

5. **Jempeng stone filter** method (used in Bali, Indonesia). This type of filtration is used when the water source is polluted by wind-borne impurities such as dry leaves, stalks, and coarse particles. The raw water is passed through a winnowing sieve, and the impurities are filtered.

Reference

1. Wastewater Recycle, Reuse, and Reclamation – vol. II - traditional and household water purification methods of rural communities in developing countries - S. Vigneswaran, M. Sundaravadivel