

MODULE 1.5

Advanced Waste Water Treatment

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MODULE 1.5

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The effluent from a typical secondary treatment plant still contains 20-40 mg/L BOD which may be objectionable in some streams. Suspended solids, in addition to contributing to BOD, may settle on the stream bed and inhibit certain forms of aquatic life. The BOD if discharged into a stream with low flow, can cause damage to aquatic life by reducing the dissolved oxygen content. In addition the secondary effluent contains significant amounts of plant nutrients and dissolved solids. If the waste water is of industrial origin, it may also contain traces of organic chemicals, heavy metals and other contaminants.

Different methods are used in advanced waste treatment to satisfy any of the several specific goals, which include the removal of (1) suspended solids (2) BOD (3) plant nutrients (4) dissolved solids and (5) toxic substances. These methods may be introduced at any stage of the total treatment process as in the case of industrial waterways or may be used for complete removal of pollutants after secondary treatment.

Removal Of Suspended Solids:

This treatment implies the removal of those materials that have been carried over from a secondary treatment settler. Many methods were proposed of which two methods were commonly used. The two methods are microstaining and chemical coagulation followed by settling and mixed media filtration.

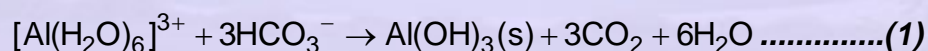
Microstraining:

It is a special type of filtration procedure which makes use of filters over from stainless steel wires with opening only 60-70 μm across to remove very small particles. High flow rates and low back pressures are normally achieved.

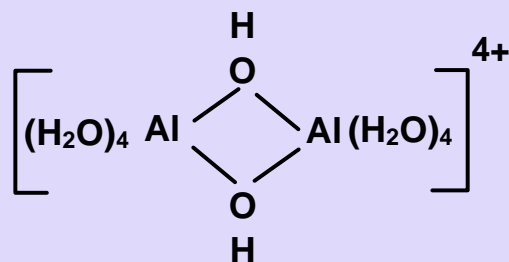
Coagulation and flocculation:

The object of coagulation is to alter these particles in such a way as to allow them to adhere to each other. Most colloids of interest in water treatment remain suspended in solution because they have a net negative surface charge that causes the particles to repel each other. The intended action of the coagulant is to neutralise that charge, allowing the particles to come together to form larger particles that can be more easily removed from the raw water.

The usual coagulant is alum $[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}]$, though FeCl_3 , FeSO_4 and other coagulants, such as polyelectrolytes, can be used. Alum when added to water, the aluminium in this salt hydrolyses by reactions that consume alkalinity in the water such as:



The gelatinous hydroxide thus formed carries suspended material with it as it settles. In addition, however, it is likely that positively charged hydroxyl-bridged dimers such as



and higher polymers are formed which interact specifically with colloidal particles, bringing about coagulation. Metal ions in coagulants also react with virus proteins and destroy upto 99% of the virus in water.

Anhydrous iron (III) sulphate can also act as effective coagulant similar to aluminium sulfate. An advantage with iron (III) sulfate is that it works over a wide range of pH.

Filtration:

If properly formed, the addition of chemicals for promoting coagulation and flocculation can remove both suspended and colloidal solids. After the flocs are formed, the solution is led to a settling tank where the flocs are allowed to settle. While most of the flocculated material is removed in the settling tank, some floc do not settle. These flocs are removed by the filtration process, which is usually carried out using beds of porous media such as sand or coal. The current trend is to use a mixed-media filter which consists of fine garnet in the bottom layer, silica sand in the middle layer and coarse coal in the top layer which reduces clogging.

Removal of dissolved solids:

The dissolved solids are of both organic and inorganic types. A number of methods have been investigated for the removal of inorganic constituents from

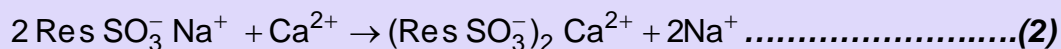
waste water. Three methods which are finding wide application in advanced waste treatment are ion-exchange, electrodialysis and reverse osmosis. For the removal of soluble organics from waste water the most commonly used method is adsorption on activated carbon. Solvent extraction is also used to recover certain organic chemicals like phenol and amines from industrial waste waters.

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.

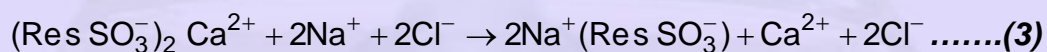
A number of naturally occurring minerals have ion exchange properties. Among them the notable ones are aluminium silicate minerals, which are called zeolites. Synthetic zeolites have been prepared using solutions of sodium silicate and sodium aluminate. Alternatively synthetic ion-exchange resins composed of organic polymer with attached functional groups such as $-\text{SO}_3^- \text{H}^+$ (strongly acidic cation exchange resins), or $-\text{COO}^- \text{H}^+$ (weakly acidic cation exchange resins) or $-\text{N}^+(\text{CH}_3)_3\text{OH}^-$ (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.



(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 Ca^{2+} and Mg^{2+} 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 as $\text{ResCOO}^-\text{H}^+$. These cation exchangers having $-\text{COOH}$ 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 .

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).

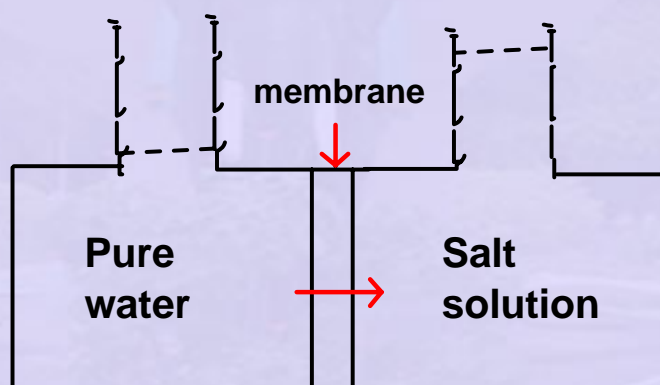


Fig 1a Osmosis

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

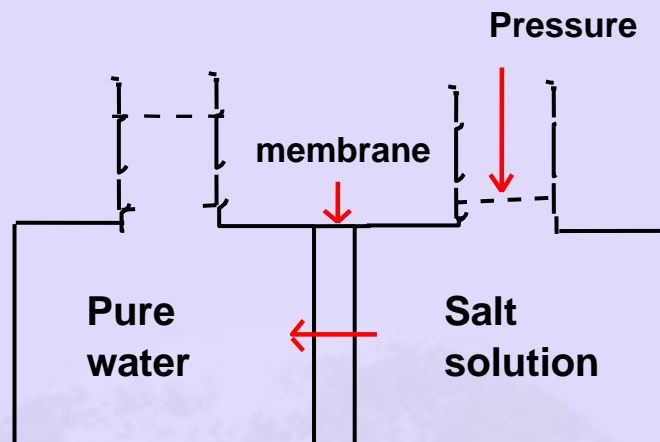


Fig 1b Reverse Osmosis

Electrodialysis:

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

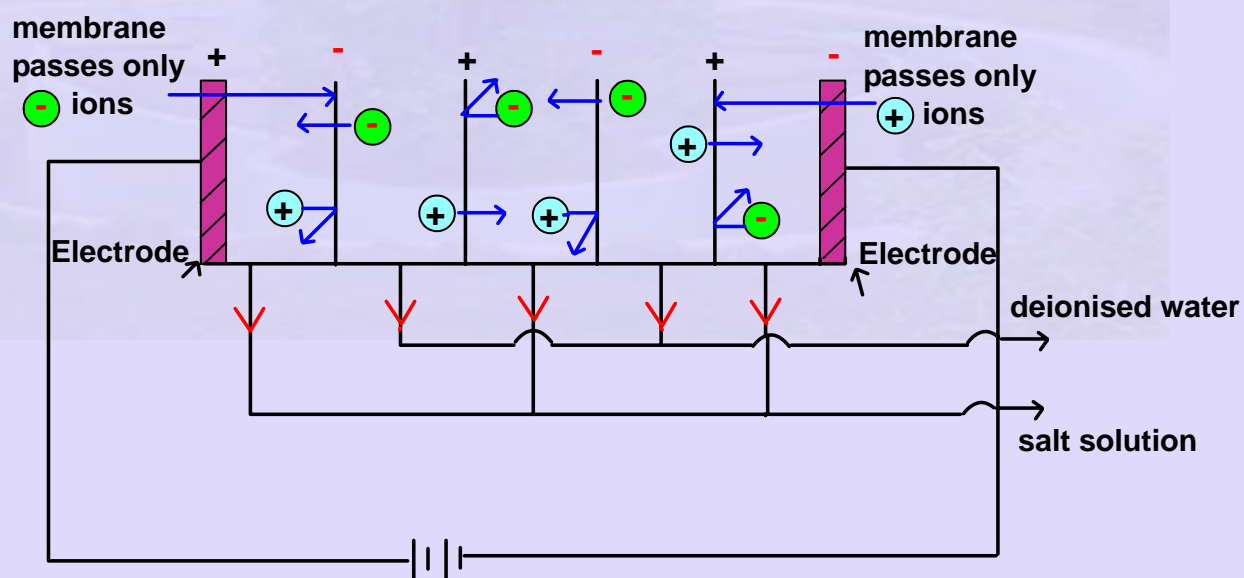


Fig.2 Electrodialysis cell

In the past electrodialysis was most often used for purifying brackish water, but it is now finding a role in hazardous waste treatment. Metal salts from plating rinses are sometimes removed in this way.

Fig.2 shows a simple dialysis cell in which waste water may be 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. 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.

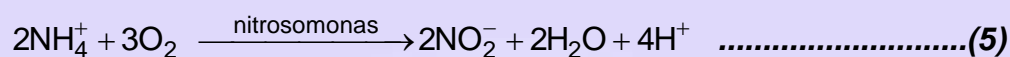
In the electrodialysis process, organic molecules are not removed and they can collect on and clog the membranes. Another disadvantage of this method is that it still leaves concentrated waste water to be disposed of by some appropriate scheme. The process does not require any chemical additives and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

Removal of nitrogen:

Nitrogen compounds may be removed in waste water in two ways. Even after secondary treatment, most of nitrogen exists as ammonia. Increasing the pH produces the reaction,

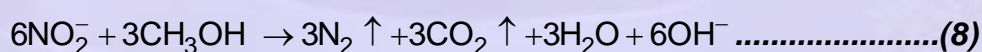
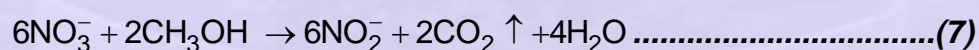


Much of the dissolved ammonia gas may then be expelled from the water into the atmosphere. The ammonium ion in the waste water may also be oxidised to nitrate by bacteria like nitrobacter and nitrosomonas, in a process called nitrification.



These reactions are slow and require long retention times in the aeration tank as well as sufficient DO. If the flow rate is too high, the slow-growing microorganisms are washed out of the aeration tank.

Once the ammonia has been oxidised to nitrate, it may be reduced by anaerobic bacteria like pseudomonas. This denitrification requires a source of carbon and methanol is often used for that purpose.



Phosphate removal (chemical treatment):

Phosphate may be removed chemically or biologically. The most popular chemical methods use lime, $\text{Ca}(\text{OH})_2$ and alum, $\text{Al}_2(\text{SO}_4)_3$. Under alkaline conditions, the calcium will combine with phosphate to form calcium hydroxyapatite, a white insoluble precipitate that is settled out and removed from waste water. Insoluble calcium carbonate is also formed and removed.



The aluminium ion from alum precipitates as very slightly soluble aluminium phosphate,



and also forms aluminium hydroxide.



which forms sticky flocs that help to settle out phosphates.

Phosphate removal (biological treatment)

Biological phosphorous removal does not require the addition of chemicals. In this process, the aeration tank in the activated sludge system is subdivided into zones, some of which are not aerated. In these zones, the aerobic microorganisms become solely stressed because of the lack of oxygen. If these microorganisms are then transferred to an aerated zone, they try to make up for lost time and assimilate organic matter (as well as phosphorous) at a rate much higher than they ordinarily would. Once the microorganisms have adsorbed the phosphorous, they are removed as waste activated sludge, thus carrying with them high concentrations of phosphorous. Using such sequencing of nonaerated and aerated zones, it is possible to remove as much as 90% of the phosphorous.

Removal of dissolved organic compounds:

Adsorption:

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 ($\sim 1000 \text{ m}^2/\text{g}$). 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°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 adsorbents are readily regenerated by solvents such as isopropanol and acetone.

Sludge treatment and disposal:

Both primary and secondary sewage treatments involve settling of particulate matter, and thus produce sludge. The concentration of solids in the primary sewage sludge is about 5%; the activated sludge contains about 1%; and the sludge from trickling filters has about 2% solids. Thus the sludge is

composed of almost entirely of water and volume reduction is the key to economic disposal. In addition to reducing its high water content, the sludge must be stabilised so that its biological activity and tendency towards putrefaction are reduced drastically.

The sludge is concentrated by gravity settling and floatation. After concentration the sludge is subjected to anaerobic digestion in a digester in which the organic content of the sludge decomposes to give mainly methane and carbondioxide and at the same time the bound water is released from the sludge.

The sludge is then conditioned to improve its dewatering characteristics by adding chemicals like iron salts and polyelectrolytes. These chemicals bind the sludge particles together and encourage the release of water. The sludge is then heated under pressure and after a period of time the gel structure of the sludge breaks down so that the water is released. The thickened sludge is then dewatered for efficient handling and disposal. The dewatering is accomplished by mechanical methods, the most common being centrifugation and filtration. The dewatered sludge is then subjected to oxidation to reduce the organic content, with the consequent destruction of bacteria and a significant reduction in their volumes. Incineration and wet oxidation are the two common methods employed for oxidation.

Several methods are employed for the ultimate disposal of sludge. The wet digested sludge may be sprayed on to a cropland where it functions as fertiliser. Dried sludge may be used a land fill or soil conditioner. Wet or partially dewatered sludge or ash from incineration may be transported from the shore to dumping grounds at sea. The potential drawback to the use of sewage sludge as fertiliser in agricultural fields is the presence of both organic and inorganic toxic

compounds. The former compounds are oxidation-resistant organic substances, such as organochlorine species which become bound in the organic matrix of the sludge. The inorganic toxicants are represented by heavy metals, mainly arsenic, cadmium, lead, mercury and zinc. These metals can be taken up by crops and introduced into the food chains or leached to the ground water.

Disinfection:

Disinfection, using chemical and physical methods is the final step in drinking water purification. The finished water is disinfected often with chlorine. It kills the remaining microorganisms in the water, some of which will be pathogenic. It is a very efficient oxidising, bleaching and disinfecting agent. In water chlorine reacts as follows:

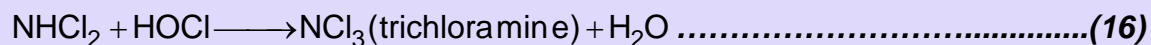
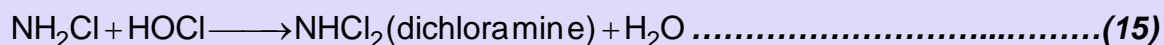


The hypochlorous acid (HOCl) is the prime disinfecting agent. Its dissociation is pH dependent yielding less effective hypochlorite ions (OCl⁻) at higher pH values:



Together, HOCl and OCl⁻ are called the free available chlorine.

A principal advantage of chlorination over other forms of disinfection is that a chlorine residual is created that can protect the treated water after leaving the treatment plant. This guards against possible contamination that might occur in water distribution system. To increase the lifetime of the residual, some systems add ammonia to the treated water, forming chloramines.



Chloramines, although they are less effective as oxidants than HOCl, are more persistent. Residual chlorine that exists as chloramine is referred to as **combined available chlorine**.

Chlorine may have adverse secondary effects. It has the potential to combine with trace amounts of organic substances to form trihalomethanes (THMs) such as the carcinogen chloroform. Some studies have shown an association between bladder and rectal cancer and consumption of chlorinated drinking water. One approach to reducing THMs is to remove more of the organics before any chlorination takes place, which can be accomplished by adsorption on activated carbon.

The problem faced with the formation of THMs has spurred interest in alternatives to chlorination as the preferred method of disinfection. Alternative disinfectants include chlorine dioxide and ozone. Chlorine dioxide (ClO_2) is a potent bactericide and viricide and it does not form a residual capable of protecting water in the distribution system. However, there is concern for certain toxic chlorate and chlorite substances that it may create, and it is a very costly method of disinfection. Ozonation involves the passage of ozone (O_3) through water.

Ozone is a very powerful disinfectant that is even more effective against cysts and viruses than chlorine, and it has the added advantage of having no

taste or odour problems. Unfortunately, the disinfective power of ozone is limited by its relatively low solubility in water.

