## **WASTEWEWATER TREATMENT**

# 11.1 Removal of Pollutants from Wastewater

Sewage is composed not only of the waste matter flushed from toilets, but also of the waste collected from all other drains in homes and other buildings. A sewer system brings all the tub, sink, and toilet drains together into larger pipelines and sewers. The final mixture from the collection system is called raw sewage or raw wastewater. Raw sewage contains about 1 part of waste in 1000 parts of water (i.e., 0.1% waste to 99.9% water). The raw sewage output in developed countries is on the order of 600–800 liters per person per day. This means that a community of 100,000 persons will produce 60-80 million liters of wastewater everyday. With storm water, raw sewage is diluted but the pollutants are nevertheless enough to darken the water and give it a foul smell.

A variety of treatments can remove organic and inorganic materials like those discussed in Chapter 8 before wastewater is discharged into surface water. They can be classified as *aerobic* and *anaerobic* processes. In general, aerobic treatments are used when the concentration of pollutants is not high (as in domestic wastewater), while the anaerobic treatment is preferred for a high concentration of organic matter (usually found in industrial sewage) as shown in Table 11.1.

These processes usually include several steps:

- · Preliminary treatment
- · Primary treatment
- · Secondary treatment

- · Tertiary treatment
- · Disinfection
- · Sludge treatment

#### 11.1.1 Preliminary Treatment

The objective of the preliminary treatment is to eliminate debris and grit. Debris includes rags, plastic bags, and other objects flushed down toilets or washed through storm drains in places where they are connected to sewers. Grit (i.e., coarse sand and gravel) also enters mainly through storm drains. As debris and grit damage or clog up pumps and some treatment processes, removing them is essential. This usually involves two steps: a screening out of debris and a settling of grit. Debris is removed by letting raw sewage flow through a bar or rotating screen and have it taken to an incinerator. A grinder called a comminute is used in some systems to reduce the debris to a relatively fine particle size which then continues through the system to be removed at a later stage.

After passing through the screen, water flows through a grit-settling tank where its velocity is slowed down just enough to allow the grit to settle, be mechanically removed, and taken to landfills. Sometimes grit chambers are aerated to prevent anaerobic processes from taking place in the dissolved and suspended organic matter.

Inert dense material such as sand, broken glass, silt, and pebbles is called grit. If these materials are not removed from the wastewater, they abrade pumps and other mechanical devices, causing undue wear. In addition, they have a tendency to settle in corners and bends, reducing flow capacity and, ultimately, clogging pipes and channels.

#### Primary treatment:

The next step after the grit removal in the wastewater treatment process is primary treatment, which involves the use of clarifiers (sedimentation tanks) to settle down the suspended solids where suspended solids and portion of the biodegradable organic matters are settled out. Primary sedimentation tanks removes 20 to 30 percent of the BOD.

Primary treatment allows the undissolved suspended solids (oil, grease and lighter solids float to the surface, suspended Solids (SS). They are too light to get settled down by the gravity to get settled. They resist removal by conventional means. For this purpose coagulants such as calcium hydroxide and aluminum sulfates (alum) are

added. Alum  $(Al_2(SO_4)_3 \cdot 18H_2O)$  forms gelatinous metal hydroxide precipitate at high pH, it eventually settle downs by gravity and it settle downs along with the suspended particles.

#### For REACTION, see class note.

Coagulation followed by filtration is a much more effective procedure than filtration alone. These settled materials are known as primary sludge and these precipitates settle down in the sedimentation tanks (primary basin) and the remaining liquid subjected to secondary treatment. Primary sludges often have a strong odor and require treatment prior to disposal.

#### 11.1.3 Secondary Treatment

The aim of the secondary treatment is to remove colloidal and dissolved biodegradable organic material. Colloidal organic material originates from the same sources as particulate organic material but has different particle size. Colloidal particles are so fine that they will not settle — at least not within any reasonable time period. Bacteria and other microorganisms (including pathogens) are also present in this category. In addition, there is dissolved organic material from soaps, detergents, shampoos, and other cleaning and washing agents.

The secondary treatment is also called biological treatment because it uses organisms—natural decomposers and detritus feeders. Basically, an environment is created to enable these organisms to feed on the colloidal and dissolved organic material, and break it down to carbon dioxide and water via their cell respiration. The sewage water from primary treatment is the food- and water-rich medium.

The activated sludge system is the process traditionally used for secondary treatment

Water from primary treatment enters a long tank equipped with an air-bubbling system. A mixture of

detritus-feeding organisms is added to the water as it enters the tank, and as it moves through the tank, it is vigorously aerated. Organisms in this well-aerated environment reduce the biomass of organic material (including pathogens) as they feed. As organisms feed on each other they tend to form clumps (flocs) that settle readily when the water is stilled.

The settled organisms are pumped back into the entrance of the aeration tank. They are the activated sludge that is added at the beginning of the process. Surplus amounts of activated sludge occur as populations of growing organisms are removed and added to the raw sludge.

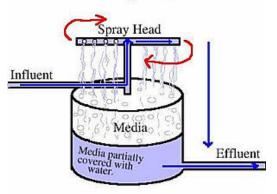
As organisms feed, they convert some organic matter and nutrients into biomass of their own bodies, while another portion is excreted as waste from respiration. Therefore, as food chains proceed toward completion, the amount of biomass may be totally reduced through metabolic processes to carbon dioxide, water, and several mineral nutrients that remain in solution.

# i) Trickling filter method:

The purpose of the trickling filter is to remove the dissolved organics. Trickling filter is simply a tank filled with a deep bed of stones or perforated plastic material (synthetic media). The most common design is a bed of stones three to ten feet deep inside a large circular concrete tank. Some tanks are more than 200 feet in diameter.

Sewage is continuously sprayed over the top of the stones from

# Trickling Filter:



rotating arms and trickles to the bottom, Bacteria gather and multiply on the stones. Microbes break down the dissolved organics, thus lowering the BOD of the sewage thereby removing contaminants. Since, this decomposition is taking place in presence of aerobic bacteria, so, to accelerate the decomposition process, air must be blown through the pipes, blowers. Air is circulated upward through the spaces among the stones providing sufficient oxygen for the metabolic processes.

Sludge is produced by this process and these sludges comprise remaining undecomposed solids found in wastewater plus organisms used in the treatment process. These sludges reach the secondary basin and collected from the bottom of the secondary basin (secondary sedimentation tank / clarifiers).



# **Sludge Treatment**

The sludge is to be treated — to stabilize the sludge and reduce odors, remove some of the water and reduce volume, decompose some of the organic matter and reduce volume, kill disease causing organisms and disinfect the sludge. The most common treatment options include anaerobic digestion and aerobic digestion.

# (i) Anaerobic digestion:

**Digestion** means substrates are heated and subjected to microbial decomposition.

Anaerobic digestion of sludge is carried out in air-tight container known as anaerobic digester. Sludges generated at primary and secondary sedimentation tank are pumped to anaerobic digesters. Most commonly, sewage sludge is subjected to anaerobic digestion ie., sludge is treated in a digester and allowing the bacterial action to occur in the absence of air.

The process can either be *thermophilic* digestion, in which sludge is fermented in tanks at a temperature of 55°C, or *mesophilic*, at a temperature of around 36°C. Though allowing shorter retention time (and thus smaller tanks), thermophilic digestion is more expensive in terms of energy consumption for heating the sludge.

Two major feature of anaerobic digestion are (i) formation of "sludge cake" and (ii) production of biogas.

- (i) After the sludge digestion, the sludge is dewatered and hence the volume is reduced. This dried sludge is called a <u>sludge cake</u>. Caustic chemicals can be added to sludge or it may be heat treated to kill disease-causing organisms. Sludge cake may be converted into fertilizer pellets and can be used as fertilizer. The product is then sold to the local market.
- (ii) Another major feature of anaerobic digestion is the production of biogas,

$$C_6H_{12}O_6 \rightarrow 3CH_4 + 3CO_2$$

During this process, some organic compounds are converted to methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) gases. The appropriate mixture of methane and carbon dioxide is known as biogas. The composition of biogas is  $\underline{50 \text{ to}}$   $\underline{75 \text{ per cent } CH_4 \text{ and } 25 \text{ to } 45 \text{ per cent } CO_2 \text{ together with minor quantities of nitrogen (< 1%), hydrogen (< 1%), ammonia (< 1%) and hydrogen sulphide (< 1%).$ 

Biogas may be used as the source of alternative energy. Like natural gas, biogas can also be used as a fuel in power generators, engines, boilers and burners. Biogas also can be utilized as cooking gas as replacement to LPG gas.

# (ii) Aerobic digestion

Aerobic digestion is a bacterial process occurring in the presence of oxygen. Under aerobic conditions, bacteria rapidly consume organic matter and convert it into carbon dioxide. Aerobic digestion can also be achieved by using jet aerators to oxidize the sludge. The operating costs used to be characteristically much greater for aerobic digestion because of the energy used by the blowers, pumps and motors needed to add oxygen to the process. However, since the recent advent of stone fibre filter technology which uses natural air currents for oxygenation, this no longer applies.

#### **Advantages of anaerobic digestion:**

- (a) Less energy is required: 0.5-0.75kWh energy is needed for every 1 kg of COD removal by anaerobic process.
- (b) Energy generation in the form of methane gas: 1.16kWh energy is produced for every 1 kg of COD removal by anaerobic process. The caloric value of the biogas is about 5.5–6.0 kWh  $m^{-3}$ . This corresponds to about 0.5 L of diesel oil.
- (c) Less sludge generation: Anaerobic process produces only 20% of sludge that of aerobic process.
- (d) <u>Production of sludge cake</u>: See above.

# **Tertiary treatment:**

#### 1. REMOVAL OF CALCIUM AND MAGNESIUM

Calcium and magnesium salts cause water hardness. And if, bicarbonate ions are present, then in the boiler, insoluble calcium carbonate is formed. Several processes are used for softening water.

a) Calcium may be removed from water very efficiently by the addition of orthophosphate followed by filtration.

$$5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{OH}^- \rightarrow \text{Ca}_5\text{OH}(\text{PO}_4)_3(s)$$

- b) On a large scale, such as in community water-softening operations, the lime-soda, Ca(OH)<sub>2</sub> process is used. Calcium is precipitated as CaCO<sub>3</sub> and magnesium as Mg(OH)<sub>2</sub>. The precipitation of magnesium as the hydroxide requires a higher pH (by adding Na<sub>2</sub>CO<sub>3</sub>)
- c) Ion exchange method.

## 2. Removal of Iron and Manganese

Soluble iron and manganese are found in many groundwaters.

The reducing conditions in groundwater favors the +2 oxidation state of these metals and Fe(II) /Mn(II) ions are soluble in water. Hence, Fe(II) is soluble in water but Fe(III) is insoluble in water.

Iron is the more common of the two metals. In groundwater, the level of iron seldom exceeds 10 mg/L, and that of manganese is rarely higher than 2 mg/L.

The basic method for removing both of these metals depends upon oxidation to higher insoluble oxidation states.

- **a.** The oxidation is generally accomplished either by aeration or by adding some oxidizing agents. Chlorine and potassium permanganate are sometimes employed as oxidizing agents for iron and manganese.
- b. Electrodeposition (reduction of metal ions to metal by electrons at an electrode),
- c. reverse osmosis,
- d. ion exchange method and
- **e.** Adsorption on activated carbon.

#### 3. REMOVAL OF HEAVY METALS

The oxidation state of the heavy metal has a strong effect upon the efficiency of metal removal. For instance, chromium(VI) is normally more difficult to remove than chromium(III).

Heavy metals → examples include cadmium, mercury, and lead. These metals get into the water body from a number of industrial processes.

**a.** Mercury, cadmium, or lead are removed by addition of sulfide as they form the precipitation of metal sulphides very easily. Once ppt is formed, it is removed by filtration technique.

$$Cd^{2+} + S^{2-} \rightarrow CdS(s)$$

- **b.** Electrodeposition  $\rightarrow$  reduction of metal ions to metal by electrons at cathode.
- c. Reverse osmosis and Ion exchange are frequently employed.

#### 4. REMOVAL OF ARSENIC

Arsenic, a toxic metalloid  $\rightarrow$  not allowed more than 10  $\mu g$  per liter of water

Arsenic usually is present in surface water as  $As(V) \rightarrow H_2AsO_4^-$  and  $HAsO_4^{2-}$ , but in groundwater, it exits as As(III).

If groundwater supplies contains the more toxic As(III) then,

- a. Chlorine, ozone, or permanganate oxidants  $\rightarrow$  to convert the As(III) to the As(V)
- b. Precipitation formation with aluminum sulfate, iron(III) salts and with lime followed by filtration effectively removes arsenic.
- c. Arsenic can also be removed from water by anion-exchange method.

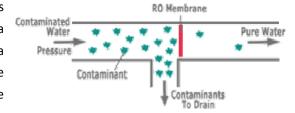
# 5. REMOVAL OF DISSOLVED INORGANICS

- a) One of the most obvious methods for removing inorganics from water is distillation. However, generally quite high energy required, so distillation is not generally economically feasible. Furthermore, volatile materials such as ammonia and odorous compounds escapes.
- b) The most effective method are electrodialysis, reverse osmosis, and ion exchange processes as they are most cost-effective.

#### **Reverse Osmosis method:**

Osmosis: The natural movement of the solvent from a region of low solute concentration to a region of high solute concentration, through a semipermeable membrane when no external pressure is applied.

**RO** (Reverse Osmosis): This is the reverse of the normal osmosis process. Pressure is applied so that water is forced to move a solvent from a region of high solute concentration through a semipermeable membrane to a region of low solute concentration. Thus, the solutes are left on one side and the pure



water on the other side. Reverse osmosis, also known as hyperfiltration, is the finest filtration available today. It is the most common treatment technology used for the purification of water. Water passes through the membrane and the solutes continue to move down, the rejected contaminants are swept away by the drain.

# 6. REMOVAL OF PHOSPHORUS

a) Chemically, phosphate is most commonly removed by precipitation ----- Chemical method.

Lime,  $Ca(OH)_2 \rightarrow most$  commonly used chemical for phosphorus removal:

$$5Ca^{2+} + 3PO_4^{3-} + OH^- \rightarrow Ca_5OH(PO_4)_3(s)$$

b) Adsorption on activated alumina, Al<sub>2</sub>O<sub>3</sub>. ---- Physical method

Activated alumina is a highly porous material; this material can have a surface area available for adsorption of contaminants (significantly over 200 square metres/g). That means it has a very high surface-area-to-weight ratio. Total surface area = surface area of pores + surface area of carbon. There exist intermolecular attractive force between the activated alumina and pollutants.

# 7. REMOVAL OF AMMONIA (NITROGEN)

Next to phosphorus, nitrogen is the nutrient most commonly removed.

Nitrogen in municipal wastewater → generally present as organic nitrogen or ammonia.

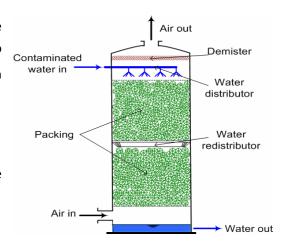
Ammonia is the primary nitrogen product produced by most biological waste treatment processes. The techniques most often used for nitrogen removal are :

#### a) Ammonia striping:

For ammonia stripping to work, the ammoniacal nitrogen must be converted to volatile NH<sub>3</sub> gas. This is done by raising the pH 10.8 to 11.5 by the addition of lime or caustic which converts ammonium ions to ammonia gas according to the following reaction(s):

$$NH_4^+ + OH^- \rightarrow H_2O + NH_3 \uparrow$$

- contaminated water is distributed over the packing in the column and water is falling downwards
- The air is entering the column and forced (there is a fan) to move upward, ie the flow of air and the water are in opposite direction
- After the addition of lime, ammonia is produced and is removed as vapor at the top of the tower (from the outlet)



- Since stripping is easier at warmer temperatures, so, sometimes heat is applied at the bottoms of the stripper. At the bottom of the tower decontaminated water is collected.
- **b)** Nitrification followed by denitrification is arguably the most effective technique for the removal of nitrogen from wastewater. This is the only biological process in the tertiary wastewater treatment.
- i) ammonia and organic nitrogen compounds are completely converted into nitrate under strongly aerobic conditions

$$2NH_4^+ + 3O_2 \xrightarrow{Nitrosomonas} 4H^+ + 2NO_2^- + 2H_2O$$
  
 $2NO_2^- + O_2 \xrightarrow{Nitrobacter} 2NO_3^-$ 

ii) The second step  $\rightarrow$  reduction of nitrate to nitrogen gas. This reaction is also bacterially catalyzed and requires a carbon source and a reducing agent such as methanol, CH<sub>3</sub>OH

$$6NO_3$$
<sup>-</sup> + 5CH<sub>3</sub>OH + 6H<sup>+</sup> (Denitrifying bacteria) →  $3N_2(g) + 5CO_2 + 13H_2O$ 

#### 8. REMOVAL OF DISSOLVED ORGANICS

- **a.** The standard method for the removal of dissolved organic material is adsorption on activated carbon. Adsorption on activated carbon treatment is the best means of removing herbicides and their metabolites from drinking water sources.
- **b.** Oxidation of dissolved organics can be accomplished by ozone, hydrogen peroxide, molecular oxygen (with or without catalysts), chlorine and its derivatives, permanganate, or ferrate (iron(VI)) can be used to destroy (break down) organic compounds.

# 9. Water disinfection

Secondary sewage effluent often contains a number of disease-causing microorganisms, requiring disinfection.

#### **Common Disinfection Agents**

(a) chlorine and chloramines; (b) bleaching powder; (c) chlorine dioxide; (d) ozone; (e) ultraviolet radiation

Chlorine and chloramines have been the mostly used but their uses becoming less because of the byproducts they produce. The use of ozone is growing; it is the **greenest** disinfection agent, because it can be made on site with air as the raw and produces few undesirable byproducts.

#### a) DISINFECTION WITH CHLORINE AND CHLORAMINES

In water chlorine, rapidly hydrolyzes

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl$$

Hypochlorous acid (HOCI) is a weak acid that dissociates

$$HOC1 \leftarrow \rightarrow H^+ + OC1^-$$

The two chemical species formed by chlorine in water, HOCl and OCl<sup>-</sup>, are known as free available chlorine. Free available chlorine is very effective in killing bacteria.

At this stage if ammonia (contaminant) is present in water, then HOCl reacts with the ammonia to form compounds called chloramines such as monochloramine, dichloramine, and trichloramine.

$$NH_4^+ + HOCl \rightarrow NH_2Cl \text{ (monochloramine)} + H_2O + H^+$$
 $NH_2Cl + HOCl \rightarrow NHCl_2 \text{ (dichloramine)} + H_2O$ 
 $NHCl_2 + HOCl \rightarrow NCl_3 \text{ (trichloramine)} + H_2O$ 

The chloramines are called combined available chlorine. These are weaker disinfectant than free available chlorine, is more readily retained as a disinfectant throughout the water distribution system.

<u>Break Point Chlorination</u> - If the water to be chlorinated contains significant amounts of ammonia, then addition of sufficient amount of chlorine will form monochloramine to di-or tri-chloramines (ie., all present ammonia is oxidized). The ratio of Cl:N at which all ammonia present in the water has been oxidized to form trichloramine is known as breakpoint ie., at breakpoint no ammonia, monochloramine or dichloramine and no free available chlorine is left in water.

If we continue further addition of chlorine, it will then only produce only free available chlorine in water. Adding chlorine to exceed the breakpoint is called breakpoint chlorination. Chlorination beyond the breakpoint ensures disinfection.

In order to reach the breakpoint, a superchlorination is applied. *To achieve this, one uses chlorine concentrations* which largely exceed the 1 mg/L concentration required for disinfection.

#### **Dechlorination:**

Over chlorination after the break point produces unpleasant taste and odor in water. The excess chlorine may be removed

(i) by filtering the over-chlorinated water through activated carbon.

(ii) by addition of a small % of SO<sub>2</sub>, Na<sub>2</sub>SO<sub>3</sub> or Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

$$SO_2 + Cl_2 + 2H_2O$$
  $\longrightarrow$   $H_2SO_4 + 2HCl$   
 $Na_2SO_3 + Cl_2 + 2H_2O$   $\longrightarrow$   $Na_2SO_4 + 2HCl$ 

#### b) Removal of microorganisms by adding beaching powder:

In small water-works, about 1 Kg of bleaching powder per 1000kiloliters of water is mixed and water is allowed to stand undisturbed for several hours. This produces hyppochlorous acid.

Ca(OCl)Cl + 
$$2H_2O$$
  $\longrightarrow$  Ca(OH)<sub>2</sub> + Cl<sub>2</sub>

Cl<sub>2</sub> +  $2H_2O$   $\longrightarrow$  HOCl + OCl (Hypochlorite ion)

#### Disadvantage:

(i) Bleaching powder introduces Ca in water, thereby making it more hard. (ii) Only calculated quantity should be used, since an excess of it gives bad taste and odor to treated water.

#### c) Ozone as disinfectant agent:

Ozone is an excellent disinfectant. Ozone is produced by passing silent electric discharge through cold and dry air. Ozone is highly unstable and decomposes spontaneously in water, according to the overall reaction,

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

The nascent oxygen is very powerful oxidizing agent and kills all the bacteria as well as oxidizes the organic matter present in water.

#### Advantage:

(i) It simultaneously removes color, odor and taste without giving any residue. Its excess is not harmful since it it unstable and decomposes into oxygen.

### Disadvantage:

(i) Quite expensive method, hence not employed for disinfection of municipal water supply.

#### d) Chlorine dioxide as disinfectant agent:

ClO<sub>2</sub> is an effective water disinfectant. It acts as oxidizing agent by the following half cell reaction:

$$ClO_2 + e^- \leftarrow \rightarrow ClO_2^-$$

In drinking water, chlorite (ClO<sub>2</sub>-) is the predominant end product that kills bacteria.

# 9. Removal of Taste and Odor:

Both organic and inorganic substances may produce taste, odor, and color in water and must be removed from

water. Experience has shown that a substance that produces an odor in water almost invariably imparts a perception of taste as well. This is not the case.

Taste, odor, and color agents can come from i) microorganisms in the water, ii) mineral substances in water, iii) salts from soil, iv) from microorganisms-degrading-organic matter in soil, and v) from chemical pollutant sources.

The most commonly reported taste and odor compounds, geosmin and MIB (2-methylisoborneol) are produced in surface water sources by naturally occurring cyanobacteria (blue-green algae). Geosmin and MIB typically produce earthy or musty tastes and odors in water streams.

**Color:** Yellow tinge indicates the presence of chromium.

Yellowish red color tinge indicates the presence of iron. Organically bound iron is a common cause of undesirable color.

Red brown color indicates the presence of peaty matter (partially decomposed vegetable matter saturated with water).

<u>Odor:</u> Disagreeable odor in water may be caused by the presence of living organisms (algae, bacteria, fungi and weeds), decaying vegetation. Besides this, there are may be chemical impurities. Iron and hydrogen sulfide are two common inorganic compounds known to produce odors in drinking water.

<u>Taste:</u> Most of the mineral substances affect water taste but do not cause odor.

Bitter taste is due to the presence of iron, aluminium, manganese, sulphate or excess of lime.

Soapy taste is due to the presence of large amount of NaHCO<sub>3</sub>.

Brakish taste is due to the presence of unusual amount of salts.

Various processes are used to remove agents that cause taste, odor, and color.

- i) Simple aeration can remove *volatile materials, such as* odorous hydrogen sulfide. Aeration may be effective for hydrogen sulfide.
- **ii)** For non-volatile metabolic products by bacteria, oxidation that destroys organics usually removes taste, odor, and color. Chlorine, Potassium permanganate, chlorine dioxide can be used.
- iii) Use of activated carbon.
- **iv)** Ozone Water Treatment : <u>Ozone</u> used by itself or with peroxide or UV has been found to be effective in removing many taste and odor compounds including geosim and MIB (1,2,3).