CHAPTER 2

THEORETICAL PART

Chapter 2
Wastewater treatment

As water is used, it becomes polluted in two ways either by domestic use or industrial use. Aquatic pollution by industry is more complex and its nature depends on industrial processes involved.

2.1 **Industrial wastewater** [8]

There are many types of industrial wastewater based on the different industries and contaminates, each sector produces its own particular combination of pollutants as shown in table (2.1).

Table 2-1 Water pollutants released by the different industrial sectors

Sector	Pollutant
Iron and steel	BOD, COD, oil, metals, acids, phenols, and cyanide.
Textiles and leather	BOD, solids, sulfates and chromium.
Pulp and paper	BOD, COD, solids, Chlorinated organic compounds.
Petrochemicals and refineries	BOD, COD, mineral oils, phenols, and chromium.
Chemicals	COD, organic chemicals, heavy metals, Suspended Solid, and cyanide.
Non-ferrous metals	Fluorine and Suspended Solid.
Microelectronics	COD and organic chemicals.
Mining	Suspended Solid, metals, acids and salts.

2.2 **Wastewater characteristics** [9]

The contaminants of major interest in wastewater and the unit operations and processes or methods applicable to the removal of these contaminants are shown in table (2.2).

Table 2-2 Unit operations and processes and treatment systems used to remove the major contaminants in wastewater

Contaminants	Unit operation, unit process or treatment System
Suspended solids	Sedimentation Screening and comminution Filtration variations, Flotation Chemical addition, Coagulation/Sedimentation Land treatment systems
Biodegradable organics	Activated-sludge variations Fixed film: trickling filters, rotating biological contactor Lagoon variations Intermittent sand filtration Land treatment systems Physical-chemical systems
Pathogens	Chlorination, Hypochlorination Ozonization Land treatment systems
Nutrients : - Nitrogen - Phosphorus	Suspended-growth nitrification and denitrification Fixed-film nitrification and denitrification Ammonia stripping, Ion-exchange Break point chlorination Land treatment systems Metal-salt addition Lime coagulation/sedimentation Biological-chemical phosphorus removal Land treatment systems
Refractory organics	Carbon adsorption, Tertiary ozonation Land treatment systems
Heavy metals	Chemical precipitation, Ion-exchange Land treatment systems
Dissolved inorganic solids	Ion-exchange, Reverse osmosis Electrodialysis, Evaporation

2.3 **Wastewater treatment methods** [9-10]

In order to achieve different levels of contaminant removal, individual waste-water treatment procedures are combined into a variety of systems, classified as primary, secondary, and tertiary waste-water treatment.

The term primary refers to physical unit operations and in some cases to chemical unit processes, secondary refers to biological unit processes, and tertiary.

The principal combination of all alternatives for wastewater treatment is shown in Figure (2.1).

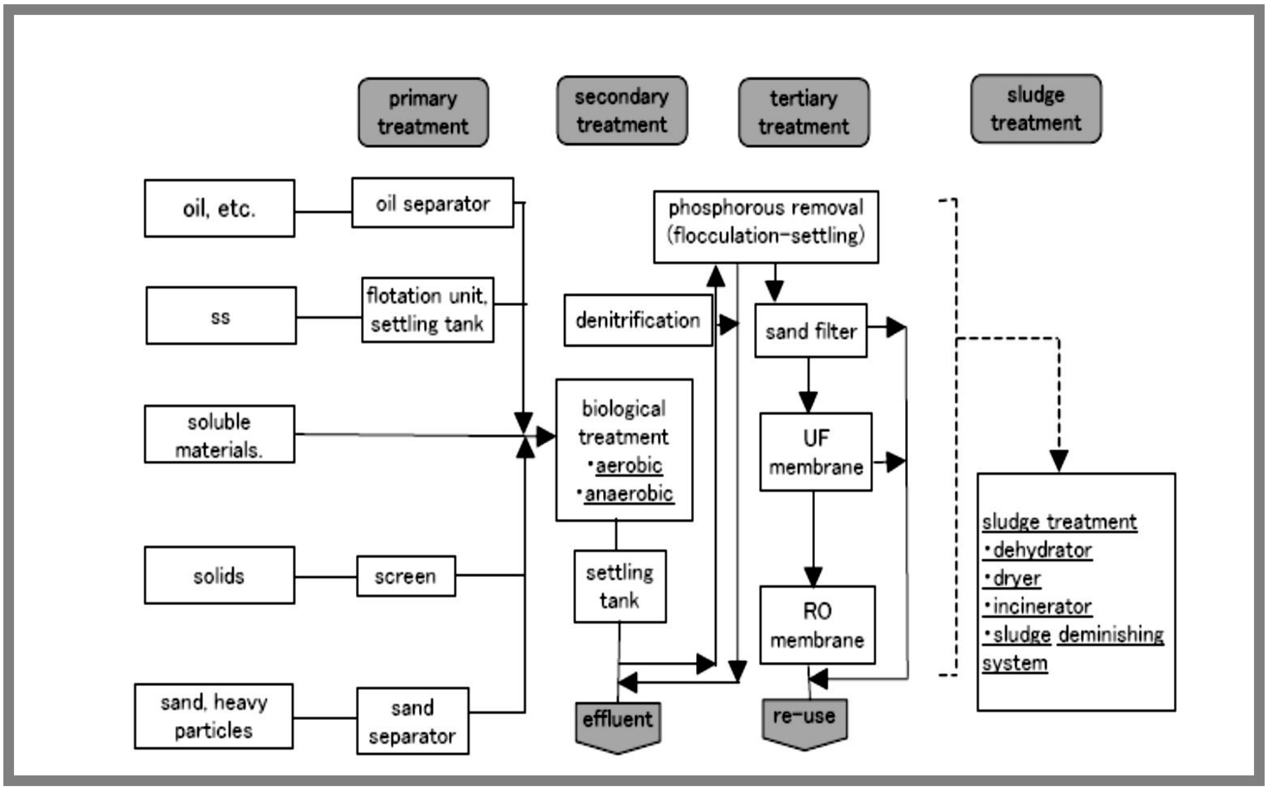

Figure 2-1 Wastewater characteristic and wastewater treatment

Wastewater treatment methods are also classified according to the type of reactions which occur during the treatment into (i) Physical treatment, (ii) Chemical treatment and (iii) Biological treatment.
In the following section a brief description of each treatment will be given.

2.3.1 **Physical Treatment**

Physical treatment or physical unit operation usually includes the following treatment techniques: cooling, equalization, screening, comminuting, grit removal, oil and grease removal, mixing, sedimentation and filtration. The principal applications of these unit operations are summarized and given in table (2.3).

Table 2-3 Application of unit operations in wastewater treatment

Operation	Application
Screening	Removal of coarse and settleable solids by interception (surface straining).
Comminution	Grinding of coarse solids to a more or less uniform size.
Flow equalization	Equalization of flow and mass loading of BOD and suspended solids.
Mixing	Mixing of chemicals and gases with wastewater, and maintaining solids in suspension.
Flocculation	Promotes the aggregation of small particles into larger particles to enhance their removal by gravity sedimentation.

Sedimentation	Removal of settleable solids and thickening of sludges.
Flotation	Removal of finely divided suspended solids and particles with densities close to that of water. Also thickens biological sludges.
Filtration	Removal of fine residual suspended solids remaining after biological or chemical treatment.
Microscreening	Same as filtration, Also removal of algae from stabilization-pond effluents.

2.3.2 **Chemical Treatment**

Those processes used for treatment of wastewater in which change is brought about by means of or through chemical reactions are known as chemical unit processes.

Chemical treatment or chemical unit processes usually includes the following treatment processes and techniques: coagulation, chemical precipitation, oxidation, reduction, ion-exchange and electrodialysis.

The chemical unit processes mentioned above and their principal applications are reported in table (2.4).

Table 2-4 Applications of chemical unit processes in wastewater treatment

Process	Application
Chemical precipitation	Removal of phosphorus and enhancement of suspended solids removal in primary sedimentation facilities used for physical – chemical treatment
Disinfection	Selective destruction of disease-causing organisms. Chlorine is the most commonly used chemical. Disinfection with ozone.
Dechlorination	Removal of total combined chlorine residual that exists after chlorination.
Others	Various other chemicals for specific objectives in WWT.

2.3.3 **Biological Treatment**

The biological wastes are rich in decomposable organic matter and can be treated by biological processes involving microbial decomposition of organic matter, aerobically or anaerobically. The main difference between aerobic and anaerobic processes is in the presence or absence of oxygen.

The common methods of biological wastewater treatment are:

a. Aerobic processes such as trickling filters, rotating biological contactors, activated sludge process, oxidation ponds and lagoons, oxidation ditches,
b. Anaerobic processes such as anaerobic digestion, and
c. Anoxic processes such as denitrification.

2.4. **Heavy Metals**

2.4.1 **Definition** [11-12]

Heavy metals are elements having atomic weight between 63.5 and 200.6, and a specific gravity greater than 5. Heavy metals which are relatively abundant in the Earth's crust and frequently used in industrial processes or agriculture are toxic to humans. These can make significant alterations to the biochemical cycles of living things.

2.4.2 **Sources of heavy metals in wastewater** [12]

Most of the point sources of heavy metal pollutants are industrial wastewater from mining, metal processing, tanneries, pharmaceuticals, pesticides, organic chemicals, rubber and plastics, lumber and wood products, etc.

2.4.3 **Examples of heavy metals and their harmful effects** [13]

Arsenic

Aside from occurring naturally in the environment, arsenic can be released in larger quantities through volcanic activity, erosion of rocks, forest fires, and human activity.

The wood preserving industry uses about 90% of the industrial arsenic in the U.S. Arsenic is also found in paints, dyes, metals, drugs, soaps and semi-conductors. Animal feeding operations and certain fertilizers and pesticides can release high amounts of arsenic to the environment as can industry practices such as copper or lead smelting, mining, and coal burning.

- Health effects and regulatory limits:

Arsenic is odorless and tasteless. Inorganic arsenic is a known carcinogen and can cause cancer of the skin, lungs, liver and bladder.

Lower level exposure can cause nausea and vomiting, decreased production of red and white blood cells, abnormal heart rhythm, damage to blood vessels, and a sensation of "pins and needles" in hands and feet and the ingestion of very high levels can possibly result in death. While the long-term low level exposure can cause a darkening of the skin and the appearance of small "corns" or "warts" on the palms, soles, and torso.

According to the Environmental Protection Agency (EPA), 0.01 parts per million (ppm) is permissible in drinking water and the Occupational Safety and Health Administration (OSHA) permits 10 micrograms per cubic meter of workplace air (10 $\mu g/ m^3$) for 8 hour shifts and 40 hour work weeks.

Barium

Barium is a very abundant, naturally occurring metal and is used for a variety of industrial purposes. Barium compounds, such as barium-nickel alloys are used for spark-plug electrodes and in vacuum tubes as a drying and oxygen-removing agent; barium sulfide is used in fluorescent lamps; barium sulfate is used in diagnostic medicine; barium nitrate and chlorate give fireworks a green color. Barium compounds are also used in drilling muds, paint, bricks, ceramics, glass, and rubber.

- Health effects and the regulatory limits:

Barium is not known to cause cancer. Short term exposure can cause vomiting, abdominal cramps, diarrhea, difficulties in breathing, increased or decreased blood pressure, numbness around the face, and muscle weakness. While large amounts of barium intake can cause, high blood pressure, changes in heart rhythm or paralysis and possibly death.

According to EPA, 2 ppm of barium in drinking water is permissible and OSHA permits 0.5 mg/m^3 of workplace air for 8 hour shifts and 40 hour work week.

Cadmium

Cadmium is a very toxic metal. All soils and rocks, including coal and mineral fertilizers, contain some cadmium. Cadmium has many uses, including batteries, pigments, metal coatings, and plastics. It is used extensively in electroplating.

- Health effects and regulatory limits:

Cadmium and cadmium compounds are known human carcinogens. Smokers get exposed to significantly higher cadmium levels than non-smokers. Severe damage to the lungs may occur through breathing high levels of cadmium.

Ingesting very high levels severely irritates the stomach, leading to vomiting and diarrhea. While long-term exposure to lower levels leads to a buildup in the kidneys and possible kidney disease, lung damage, and fragile bones.

According to EPA, 5 parts per billion (ppb) or 0.005 ppm of cadmium in drinking water. While Food and Drug Administration (FDA) recommends that the concentration in bottled drinking water should not exceed 0.005 ppm (5 ppb) and OSHA permits an average of 5 $\mu g/m^3$ of workplace air for an 8-hour workday, 40-hour work week.

Lead

As a result of human activities, such as fossil fuel burning, mining, and manufacturing, lead and lead compounds can be found in all parts of our environment. This includes air, soil, and water. Lead is used in many different ways. It is used to produce batteries, ammunition, metal products like solder and pipes, and X-ray shielding devices. Lead is a highly toxic metal and, as a result of related health concerns (see below), its use in several products like gasoline, paints, and pipe solder, has been drastically reduced in recent years. Today, the most common sources of lead exposure in the United States are lead-based paint and possibly water pipes in older homes, contaminated soil, household dust, drinking water, lead crystal, lead in certain cosmetics and toys and lead-glazed pottery.

- Health effects and regulatory limits:

EPA has determined that lead is a probable human carcinogen. Lead can affect every organ and system in the body. Long-term exposure of adults can result in decreased performance in some tests that measure functions of the nervous system; weakness in fingers, wrists, or ankles; small increases in blood pressure; and anemia.

Exposure to high lead levels can severely damage the brain and kidneys and ultimately cause death. While in pregnant women, high levels of exposure to lead may cause miscarriage.

EPA recommends 15 ppb of lead in drinking water and 0.15 $\mu g/m^3$ in air.

Mercury

Mercury combines with other elements to form organic and inorganic mercury compounds. Metallic mercury is used to produce chlorine gas and caustic soda, and is also used in thermometers, dental fillings, switches, light bulbs, and batteries. Coal-burning power plants are the largest human-caused source of mercury emissions to the air in the United States. Mercury in soil and water is converted by microorganisms to methyl mercury, a bioaccumulating toxin.

- Health effects and regulatory limits:

The EPA has determined that mercuric chloride and methyl mercury are possible human carcinogens.

The nervous system is very sensitive to all forms of mercury. Exposure to high levels can permanently damage the brain, kidneys, and developing fetuses. Effects on brain functioning may result in irritability, shyness, tremors, changes in vision or hearing, and memory problems.

Short-term exposure to high levels of metallic mercury vapors may cause lung damage, nausea, vomiting, diarrhea, increases in blood pressure or heart rate, skin rashes, and eye irritation.
EPA recommends 2 ppb in drinking water and FDA permits 1 ppm of methyl mercury of seafood. While OSHA recommends 0.1 mg/m^3 of mercury in workplace air and 0.05 mg/m^3 of metallic mercury vapor for 8-hour shifts and 40-hour work week.

Selenium

Selenium is a trace mineral widely distributed in most rocks and soils. Processed selenium is used in the electronics industry; as a nutritional supplement; in the glass industry; in plastics, paints, enamels, inks, and rubber; in the preparation of pharmaceuticals; as a nutritional feed additive for poultry and livestock; in pesticide formulations; in rubber production; as an ingredient in antidandruff shampoos; and as a constituent of fungicides. Radioactive selenium is used in diagnostic medicine.

- Health effects and regulatory limits:

Selenium is toxic in large amounts, but trace amounts of it are necessary for cellular function in most, if not all, animals. For humans, selenium is an essential trace nutrient. For example, selenium plays a role in the element functioning of the thyroid gland. The tolerable upper intake level is 400 micrograms of selenium per day.
Short-term oral exposure to high concentrations can cause nausea, vomiting, and diarrhea. Chronic oral exposure to high concentrations can produce selenosis. Major signs of selenosis are hair loss, nail brittleness, and neurological abnormalities. Brief exposures to high levels in air can result in respiratory tract irritation, bronchitis, difficulty breathing, and stomach pains. Longer-term exposure can cause respiratory irritation, bronchial spasms, and coughing.
According to EPA, 50 ppb of selenium in drinking water is recommended and OSHA permits 0.2 mg/m^3 in workroom air for an 8-hour work shift.

Silver

Silver usually combines with other elements such as sulfide, chloride, and nitrate. Silver is used to make jewelry, silverware, electronic equipment, and dental fillings. Silver metal is also used in electrical contacts and conductors, in brazing alloys and solders, and in mirrors. Silver compounds are used in photographic film. Dilute solutions of silver nitrate and other silver compounds are used as disinfectants and as an antibacterial agent. Silver iodide has been used in attempts to seed clouds to produce rain.

- Health effects and regulatory limits:

According to EPA, silver is not classifiable as a human carcinogen.
Exposure to high levels for a long period may result in a condition called argyria, a blue-gray discoloration of the skin and other body tissues. Argyria appears to be a cosmetic problem that may not be otherwise harmful to health.
Exposure to high levels of silver in the air has resulted in breathing problems, lung and throat irritation, and stomach pains.
Skin contact with silver can cause mild allergic reactions such as rash, swelling, and inflammation in some people.
EPA recommends concentration in drinking water not to exceed 0.1 ppb. Requires that spills or accidental releases of 1,000 pounds or more be reported. OSHA permits in workplace air, 0.01 mg/m^3 for an 8-hour workday, 40-hour workweek.

Chromium

Chromium is found in rocks, animals, plants, and soil and can be a liquid, solid, or gas. Chromium compounds bind to soil and are not likely to migrate to ground water but, they are very persistent in sediments in water. Chromium is used in metal alloys such as stainless steel; protective coatings on metal (electroplating); magnetic tapes; and pigments for paints, cement, paper, rubber, composition floor covering and other materials. Its soluble forms are used in wood preservatives.

- Health effects and regulatory limits:

Chromium (VI) compounds are toxins and known human carcinogens, whereas Chromium (III) is an essential nutrient.

Breathing high levels can cause irritation to the lining of the nose; nose ulcers; runny nose; and breathing problems, such as asthma, cough, shortness of breath, or wheezing.

Skin contact can cause skin ulcers. Allergic reactions consisting of severe redness and swelling of the skin have been noted.

Long term exposure can cause damage to liver, kidney circulatory and nerve tissues, as well as skin irritation.

According to EPA, 0.1 ppm of chromium (VI) in drinking water is recommended. While FDA recommends that chromium (VI) should not exceed 1 ppm in bottled water and OSHA permits an average of between 0.0005 and 1.0 mg/m^3 of workplace air for an 8-hour workday, 40-hour workweek, depending on the compound.

2.5. **Removal of Hexavalent Chromium from Contaminated Water and Wastewater**

The Cr(VI), appears to be one of the major heavy metal pollutants globally in this century. Cr(VI),derived from industrial wastewater, is highly toxic and present a serious threat to human health and environment. Cr(VI) removal was evaluated at different conditions, such as pH, initial chromium concentration, temperature. Various chromium-contaminated water such as ground water, drinking water, tannery wastewater, electroplating wastewater, and synthetic industrial wastewater. Adsorption is relatively new practice for the removal of chromium. It has been a useful tool for controlling the extent of metal pollution. Activated carbons are expensive and can remove a few milligrams of metal ions per gram of activated carbon, and there are still some problems encountered in the regeneration process. Biosorption is a relatively new process that has proven very promising in the removal of chromium ions from aqueous effluents. Chitosan is a good adsorbent for Cr(VI) because of its high hydrophilicity, large number of primary amino groups and flexible structure of polymer chain. Chemical modification in general improved the adsorption capacity of adsorbents probably due to a higher number of active binding sites after modification, better ion-exchange properties, and formation of new functional groups that favors chromium uptake. Membrane filtration is another removal technique. Membranes can treat inorganic effluent with a high Cr(VI) concentration. Depending on membrane characteristics, membrane filtration system can remove chromium at a wide range of operational conditions. Despite the advantages, ion exchange also has some limitations in treating wastewater laden with heavy metals such as Cr(VI). In addition, suitable ion exchanger resins are not available for all heavy metals, the capital and operational cost is high. Another technique that was discussed for removal of Cr(VI) was electrochemical treatment with the advantage of low-cost and high selectivity. Selection of a suitable technique depends on initial Cr(VI) concentration, plant flexibility and reliability, environmental impacts and economic consideration and operational cost.