

Chapter I

Introduction

Water is life's matter and matrix, mother and medium. There is no life without water.

- *Albert Szent-Gyorgyi*

Earth, the only one water planet in our solar system is covered with water to nearly three quarters of the earth's surface. Water plays a critical part in all aspects of life – in the food security, national environment, economics, politics and production. About 90% of water is oceanic, 2% as frozen ice polar region and remaining 1% is available in the form of fresh water in lakes, streams, rivers and groundwater¹. India has 2.4% region of the earth and 2.5% of world's fresh water assets with 17% of global population to support among its limited resources. Out of entire fresh water, more than 50% is consumed by industries activity and the remaining portion is used for drinking/municipal and irrigation purpose.

1.1 Importance of Water

Water, being an indispensable resource, is considered as the elixir of life. Human physiology shows more than two third of body's weight is contributed by water which is inevitable for normal and healthy growth of our life. The essentiality of water extends to drinking, cooking, growing food, irrigation, washing clothes, bathing, recreation, industry, mining shipping, as well as generation of electric power.

In India, more than 75% of population depends on agronomy for their livelihood. Agriculture sector is the greatest user of water, where about 70% of irrigated water is discharged as runoff or wasted as inefficient irrigation system. For primary fuels, water is utilized for fuel refining, processing and resource extraction.

Large quantities of water are also used in oil refineries, heat exchanger systems and the steam turbine². According to the World Bank, water demand in the power generation sector will raise from 67 - 228 billion m³ in 2025³. This is due to the exponential increase of population, and depletion of water table from underground sources considerably⁴.

Unequal distribution of rain water and occasional drought, excessive exploitation of groundwater sources and its insufficient recharge, deterioration of water quality due to indiscriminate discharge of both domestic and industrial effluents without adequate treatment⁵, shall be considered as the factual reasons for reduction of water resources. This affects the per capita availability of water resulting in acute water scarcity.

1.2 Water Quality Parameters/ Assessment

Water, drinking water and potable drinking water are the various terms to be judiciously coined these days in the context of alarmingly higher rate of water contamination by organic compounds, heavy metals, non-metals and pathogenic micro-organisms. Water received by cities, towns and villages through the so called protected water supply schemes are supposed to be the safe drinking water. On the other hand, water is also the source several of waterborne diseases due to the presence of these micro-organisms, organic and inorganic ions entering the life system.

The essential requirements of drinking or potable water are of

- Sparkling clear and odourless
- Pleasant in taste
- Turbidity not exceed 10 NTU
- Free from objectionable dissolved gases like oxides of sulphur/ nitrogen, hydrogen sulphide and minerals such as arsenic, lead, manganese and chromium salts
- Total dissolved solids < 500 mg/L
- Total organic content < 5 mg/L
- Dissolved salts: 50-500 mg/L
- Free from disease producing microorganisms.

The presence of inorganic minerals in water can be classified as:

- Minerals required daily in large quantities. e.g. K, Ca, Na and Mg
- Elements in smaller quantities. e.g. Co, Cu, Mn, Fe, Zn and Mo
- Toxic elements at very low concentration. eg: Ag, As, Bi, Be, Hg, Cd and Pb.

1.3 Water Pollution

Water pollution is the major environmental problem. About 70 % of the groundwater and surface water are contaminated by chemical, biological, inorganic,

organic and toxic pollutants. Polluted water is not only unfit for drinking, also unsuitable for industrial and agricultural purposes. It is detrimental to plants, animals, human beings, birds and fish. The health implications of poor water quality are enormous with sanitation related diseases, which are responsible for the 60 % health burden.

1.3.1 Causes of Water Pollution

The contaminants that led to water pollution include:

- Industrial activity, where both solid wastes and effluents are let off into ground water/ freshwaters. Few prevalent contaminants water are mercury, lead, asbestos and petrochemicals
- Sewage let off from domestic households, commercial buildings disposed in an untreated manner into the sea. Sewage pollutants mainly include flush chemicals and pharmaceuticals
- Solid waste dumping and littering of plastics, cardboard, Styrofoam, glass, tins, aluminum etc., into the water bodies
- Oil spills from tankers and ship travel. Oil, being insoluble in the water, makes the surface water translucent, thereby hinders the penetration of sunlight, affecting aquatic organisms
- Burning of fossil fuels and industrial/ motor vehicles emissions their fusion with water vapor resulting in acid rain
- Temperature increase in water bodies due to discharge of cooling waters from thermal plants.

1.3.2 Classes of Water Pollutants

i. Physical Pollutants

The pollutants include excessive sediment load, temperature change and garbage dumping out of domestic activities. The thermal stratification leads to the temperature rise thereby reducing the DO content of water, where reflects upon the aquatic fauna in adverse ways.

ii. Chemical Pollutants

Chemical contaminants are generally atoms / molecules, which have been discharged into natural water streams, usually by activities of human beings. Common examples are mercury emanating due to mining activity, certain nitrogenous compounds employed in agriculture, chlorinated organic molecules from sewage/ water treatment plants and acid discharges from various manufacturing activities.

iii. Radioactive Pollutants

Radioactive pollutants originate from the following

- Mining and processing of ores
- Use in research, medical, agriculture and industrial activities, such as P^{32} , I^{131} , Co^{60} , S^{35} , Ca^{45} , C^{14} , etc.
- Radioactive discharge from nuclear power plants and nuclear reactors, e.g., U^{238} , U^{235} , Cs^{137} , Sr^{90} , Pu^{248}
- Uses and testing of nuclear weapons

These isotopes are toxic to the life forms; they accumulate in the bones, teeth and can cause serious syndromes. The safe concentration for lifetime consumption is $1 \times 10^{-7} \mu$ curies/ mL.

iv. Pathogens

The pathogenic microorganisms enter into the water body through sewage discharges as a major source or through slaughterhouses. Viruses and bacteria can cause water borne diseases such as typhoid, cholera, polio, dysentery and hepatitis in humans.

1.3.3 Sources

Factors that contribute the water pollution can be categorized into two different groups

- Point sources
- Non-point sources

i. Point Sources

When the source of pollution is single, well identified and produce significant amount of pollutants such source is known as point source (Figure 1.1). Point sources of water pollution include discharge from municipal sewage and industrial plant. Pollution from agriculture may include animal waste lagoons, animal feeding operations, mixing, storage/ handling and cleaning areas for, fertilizers, pesticides and petroleum. Municipal point sources might include landfills, motor pools, utility stations, wastewater treatment plants and fleet maintenance facilities.

ii. Non-Point Source

Nonpoint-source pollution occurs as water moves through the ground and gathers the natural and human-made pollutants, which can be deposited in rivers, lakes, coastal waters, wetlands and even groundwater (Figure 1.2). The water carries nonpoint-source pollution may originate from natural processes such as rainfall, snowmelt and human activities such as crop irrigation or lawn maintenance. The most common nonpoint-source pollutants are nutrients, sediment, microorganisms and toxics.



Figure 1.1 Point Source



Figure 1.2 Non- Point Source

1.4 Heavy Metal Pollution

The groups of transition (III A and B) and post transition elements are referred to as heavy metals, which include lead, copper, cadmium, chromium, mercury, zinc, nickel, manganese and the metalloids arsenic and selenium. Most of these elements are classified as priority pollutants by the United States Environmental Protection Agency (USEPA)

and have been grouped under dangerous substances by the CEC [Commission of European Communities]. These metallic elements are an intrinsic component of the environment and a variety of natural processes are responsible for their widespread occurrence at trace levels in various parts of the biosphere. On an annual basis, significant quantities of various heavy metals are produced from the mining of their respective ores. Industrial uses of metals and other domestic processes have introduced substantial amounts of potentially toxic metals into the atmosphere, aquatic and terrestrial environs. In particular, the effluents from paper and pulp, leather, textile, tannery, electroplating, refining, pigment, paint, dyes and galvanizing operations both on small and large-scales contain considerable amounts of toxic metal ions. The risks of these metals are prioritized in the table 1.1.

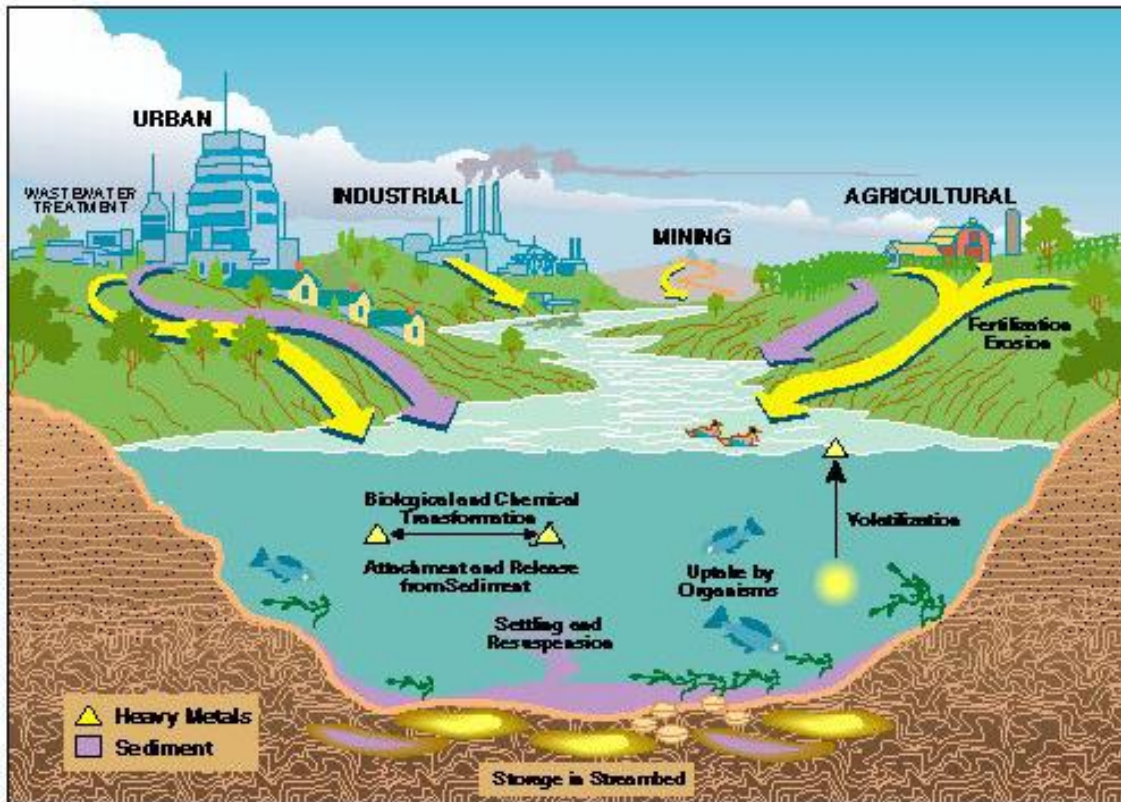


Table 1.1 Significant Anthropogenic Sources of Heavy Metal Pollution⁶

Heavy Metals	Sources
Lead (Pb)	Batteries, smelting operation, paint pigments, bangle industry, pesticides, PVC plastics, crystal glass, ceramics, E- waste, X-ray shielding, auto mobile exhaust
Cadmium (Cd)	Batteries, fertilizers, fungicides, insecticides, dental alloy, tobacco smoke, electroplating, E- waste, automobile exhaust, paints, PVC plastics
Nickel (Ni)	Electro plating, diesel oil, coins, stainless steel, smelting operations, coal, thermal power plants, battery, magnets
Copper (Cu)	Industrial, domestic wastes and metal plating, paper and pulp, mineral leaching, tailings, chemicals, mining, smelting operation, slag heaps, electronics, electrical goods, utensils
Chromium (Cr)	Alloys, dyes and pigments, wood preservatives, leather tanning, electroplating
Cobalt (Co)	Automobile exhaust, glass enamel, steel, coal, alloys, electroplating
Zinc (Zn)	Ointment, paint, rubber, smelting, paper, dye, wood preservative, electroplating
Iron (Fe)	Medicines, pipes, machinery, cookware, dye, textiles

Environmental Risk of Metals

Relative Priority	Associated Metal
High	Pb, Cd, Hg
Medium	Co, Cu, Ni, Cr, Zn
Low	Fe, Al

1.5 Heavy Metals Causing Pollution

The source and toxicity of some heavy metals are detailed below.

1.5.1 Lead (Pb)

Lead is a naturally occurring soft, bluish-white metal found in small amounts in the earth's crust having no characteristic taste or smell. Its chief employment includes: lead accumulator, alloys, plumbing and paint industries.

Lead (Pb) by complexing with oxo groups in enzymes, virtually affects all steps in the process of haem synthesis and porphyrin metabolism⁷. Lead soldering contaminates drinking water where it is used to connect the plumbing system⁸. Lead is also found in pewter pitchers, dinnerware, toys, storage batteries, and hobbies involving soldering such as jewelry making, pottery glazing, stained glass, paint sets supplies and miniature lead figures.

Most of lead used by industry comes from mined ores or from recycled scrap metal or batteries. Human activities have spread lead and these substances that contain lead to all parts of the environs. The secondary sources of lead pollution are battery manufacturers, paper and pulp industries, lead smelters, paint, ship fuels and ammunition industries. In addition, the manufacture of television picture tubes, petroleum fuels, pigments, printing, glass industries, photographic materials, etc., also forms the basis of lead pollution.

Lead can travel to the central nervous system directly from the intestinal tract by absorption^{9, 10}. The half-life period of Pb in blood is \approx 16 to 40 days and in bones about 17 to 27 years (1990, EPA). Low levels of Pb have been identified in patients with anemia, causing damage to the blood forming systems while high levels lead to severe dysfunction of the liver, kidneys, the peripheral and central nervous system. Lower IQ values and other neuro-psychological deficiencies among the children are due to exposure of higher lead levels.

1.5.2 Cadmium (Cd)

Cadmium is a silvery-white, lustrous, but tarnishable, soft, ductile divalent metal. Chemically it occurs in combination with Zinc ores through isomorphism replacement⁹. It is an uncommon, evenly prevalent element in an average concentration lying between 0.15 - 0.2 mg/ kg, occurring in the form of inorganic compounds and complexes with chelating agents¹¹.

The concentration of this element is observed to be at a minimum of 0.001 mg/ L in fresh water and 0.00015 mg/ L in seawater. Vegetative plants contain this element, the reason could be the uptake through roots and aerosol deposition in leaves¹². It is not an essential nutrient for animals or humans. However, the main sources of Cd pollution are

through industrial wastes viz., Ni- Cd, Ag- Cd, solar batteries, electroplating, paint pigments, plastics, transportation equipment, machinery/ baking channels, photography and municipal discharges¹³. Usage of cadmium is growing steadily at an annual rate of 5 to 10% and their production is reported to be 20,000 tones.

Cadmium is highly toxic even in a small quantity, leading to high blood pressure, heart diseases and even death¹⁴. Acute exposure to the fumes may result in pulmonary diseases, renal tube damage and prostate cancer¹⁵. The harmful effects of cadmium also include hypertension, respiratory disorder, aminoaciduria, osteoporosis and glycosuria¹⁶.

Cigarette smoke has high level of Cd leading to local air pollution as affecting the secondary sources. A disease specially associated with cadmium poisoning was recognized in Japan, called Itai-itai¹⁷. This was due to the consumption of cadmium contaminated rice. The disease was characterized by kidney malfunction; drop in the phosphate level of the blood serum, loss of minerals from the bones, bone fracture and intense pain.

1.5.3 Nickel (Ni)

Nickel is the 24th abundant element. It occurs as sulphides and oxides deposits¹⁸. Wastewaters rich in nickel enter water streams from the varied industrial sources viz., nickel plating, zinc base coating, silver refineries, porcelain enameling, storage batteries, mineral processing¹⁹.

Nickel is also found in tea, cocoa, peanuts and several other foodstuffs. The tolerable daily intake is 300 to 600 micro gram/ day²⁰. It is an essential micro nutrient for microorganisms and animals. It is associated with the synthesis of vitamin B₁₂.

Nickel-itch and respiratory disorders caused due to nickel pollution are prime toxic effects. Dermatitis is observed in women, wearing nickel jewelry²¹. Apart from this, excess Ni(II) concentration in polluted waters lead to acute adversity to organs like kidneys, lungs affecting intestines, bringing in about renal edema²². Nickel carbonyl has been estimated as lethal to humans at an atmospheric exposure of 30 mg/ L for 30 minutes²³.

1.5.4 Chromium (Cr)

The most common oxidation levels of Cr are +6, +3 and +2. In nature, Chromium is found in the form of complex cubic isomorphous minerals called Spinel²⁴. Prevalent

valencies of Chromium are +3 and +6 states. Cr is a rare industrial metal which is greyish-white in colour, very hard and has a high resistance to corrosion. Industrial applications of chromium compounds include pigments, leather tanning, electroplating, metal finishing, magnetic tapes, chemical manufacturing, brass, wood protection, electrical and electronic equipment, catalysis²⁵. An invisible oxide coating on the surface of Cr helps to maintain its brightness. This property allows Cr to become a protective and a decorative coating for other metals such as bronze, brass and steel. Chrome plating process is employed in the automobile parts such as bumpers of vehicles²⁶.

Stainless steel is an alloy of iron, typically containing 18% Cr, 8% Ni with or without small amounts of molybdenum and silicon. Chrome steel contains a higher concentration of chromium but no nickel, with possibly small amounts of carbon, manganese, phosphorus, silicon and sulphur depending on the alloy. Chrome steel alloys provide high corrosion resistance and good hardenability. Cr^{3+} is an essential trace element for metabolism²⁷.

Excessive inhalation of Cr^{6+} leads to dermatitis, gastric cancer and perforation of the nasal septum in its workers. It can also damage liver and kidney, cause respiratory problems, irritation and ulceration. Acute exposure to Cr^{6+} develop lethal symptoms: vomiting and persisting diarrhea, rapid hemorrhagic diathesis/ epitaxis and then convulsions as a final stage of illness²⁸.

Table 1.2 Permissible Limits of Toxic Metals Contaminants

Metals	Drinking Water	Industrial Effluent Discharge			
	BIS	International Standard		Indian Standard	
		USEPA	WHO	Into Public Sewers	Inland Surface Water
	mg/L	µg/L	µg/L	mg/L	mg/L
Nickel	0.10	-	2	3.00	3.00
Cobalt	1.07	-	-	0.60	0.25
Lead	0.05	5	10	1.00	0.10
Chromium	0.05	100	50	2.00	0.10
Zinc	5.00	-	-	15.0	5.00
Copper	0.06	1300	-	3.00	3.00

1.6 Treatment Strategies for Heavy Metal Ion Removal

It is essential to appraise the quality of water on a continuous basis due to its ever increasing demand in the municipal and industrial applications. The purpose of wastewater treatment is to remove the pollutants, so that the treated water meets the acceptable quality standards. This usually depend on, whether the water is to be reused or discharged into a receiving stream²⁹. Finding appropriate remedial measures for the wastewater treatment is a complex task involving considerations of many factors: reliability of the process equipment, desired quality of treated water, space available for the construction of treatment facilities, waste disposal constraint and implementation. The treatment of wastewater to make it suitable for subsequent use constitutes physical, chemical and biological processes³⁰.

1.6.1 Biological Treatment Process

Biodegradation methods such as fungal decolorization, microbial degradation, adsorption by microbial (living or dead) biomass and bioremediation systems are commonly applied for the treatment of industrial effluents^{31, 32, 33}. Bacteria, algae, yeast and fungi are the important biomasses which have been most widely studied for their ability to degrade pollutants such as metal ions and dyes.

1.6.2 Anaerobic- Aerobic Activated Sludge Process

It is a suitable method for removing heavy metal ions from the wastewater. Chromium VI can be biologically removed by fresh activated sludge acclimation³⁴. Aerobic and anaerobic activated sludge were used for the removal of Cu(II), Zn(II), Mn(II) and Fe(III) ions from aqueous solution³⁵. Heavy metals such as copper (Cu), lead (Pb), zinc (Zn), manganese (Mn), iron (Fe), boron (B), arsenic (As), molybdenum (Mo), and vanadium (V) were leached from aerobic and anaerobic landfill bioreactor test cells. Continuous-flow AS-biofilm pilot-plant has been used to remove the cadmium, zinc and nickel by conducting a series of biosorption batch tests and biosorption capability of biomass have been evaluated³⁶. Biological process has many drawbacks like longer detention time, less resistant to recalcitrants and longer acclimatization phase.

1.6.3 Chemical Treatment Process

Chemical treatment process consists of using certain chemical reaction or reactions to improve the water quality. The most commonly used chemical processes are ozonation, precipitation, ion-exchange, electro-coagulation, etc.

i. Ozonation

Ozone is an extremely powerful oxidant and is to be an efficient disinfectant. Ozone reacts in aqueous solution with various organic and inorganic compounds, either by direct oxidation of molecular ozone or through secondary radical type reaction involving hydroxyl radical produced by the decomposition of ozone in water³⁷. The removal of heavy metal ions by ionization, pyridine and formaldehyde in combination with UV radiation has been reported³⁸.

ii. Precipitation

Precipitation is one chemical process by which metals and dyes are removed from water. Chemical precipitation is more widely known as precipitation softening. It is used to remove or reduce the hardness in potable waters loaded with calcium and magnesium ions. Addition of alkaline reagents such as, limestone, lime, ferrous salts or other compounds are commonly used to raise the pH of acidic water to alkaline then heavy metals are removed by precipitation^{39, 40}.

iii. Ion-Exchange

Ion-exchange has been extensively used to remove hardness, iron and manganese salts from drinking water. It has also been used to selectively remove specific impurities, and to recover valuable trace metals (chromium, copper, lead, cadmium, nickel, etc.,) and dye molecules from industrial waste discharges. An ion exchanger is a resin capable of exchanging either cations or anions from the surrounding materials. Ion-exchange resins are available selectively for certain metal ions. Cation exchange resins are synthetic polymers containing an active functional group, such as the sulphonic acid (SO_3H) and other groups like carboxylic acid ($-\text{COOH}$). Natural materials such as zeolites^{41, 42} can also be used as ion exchange media to exchange cations from wastewater. Inglezakis⁴³ *et al.* investigated the effect of competitive cations and anions on ion exchange of heavy metals on clinoptilolite.

iv. Electro-Coagulation

Contaminants present in wastewater are maintained throughout the solution by electrical charges. Electro-coagulation is an electrochemical process; electrical current is employed to remove heavy metals from a solution. This system is effective in removing suspended solids, dissolved metals, tannins and dyes. When these ions and other charged particles are neutralized with ions of opposite electrical charges provided by the electro-coagulation system, they become destabilized and get precipitated in a stable form⁴⁴.

1.6.4 Physical Treatment Process

Physical treatment processes are based on the physical properties of the contaminants and are generally simpler form of all treatment processes. Physical treatment processes such as floatation, reverse osmosis, adsorption etc., and for the removal of heavy metal ions from aqueous solution.

i. Flotation

Suspended particles can be removed by allowing them to float on the surface, because they have lesser specific gravity than water. This can be done passively using gravity floatation or assisted using air and dissolved air floatation (DAF). Zn(II), Ni(II) and Cu(II) were removed using air floatation process, thereby natural zeolite (chabazite)⁴⁵ rich in Na⁺, K⁺, Ca²⁺ were exchanged with metal ions.

ii. Reverse Osmosis

Reverse osmosis (RO) is one of the physical treatment processes that uses a semi-permeable membrane for the removal of salts, metal ions and dyes by diffusion controlled transport, a mechanism where one molecule at a time diffuses through vacancies in the molecular structure of the membrane material. Osmosis is the movement of water (or any solvent) from a dilute to a concentrated solution through a semi-permeable membrane. If the membrane is placed between freshwater and saltwater, the solvent (i.e. pure water) will move through the membrane until the salt concentration on either side becomes equal. Only water can pass through the membrane and the salts are retained. The movement of water across the membrane is caused by a difference in pressure and continues until the pressure at both sides becomes equal, limiting further passage. The pressure differences

which cause the occurrence of osmosis to occur is known as the osmotic pressure. RO uses this principle to make the solvent move from the concentrated to the dilute solution side by exerting higher pressure than the osmotic pressure on the concentrated solution, thus reversing the direction of flow across the membrane^{46, 47}.

A review of the various physical, chemical and biological methods to remove metal ions reveal that they possess their own drawbacks, viz., economically unfeasible; incomplete removal of the targeted metal ions, dyes and their organic metabolites due to colour fastness, stability and the resistance of dyes to degradation. The afore mentioned treatment methods possess some advantages but they are backed by some of the disadvantages like generation of a significant amount of sludge causing secondary pollution problems; substantial increase in the cost of these treatment methods involving complicated procedures^{48, 49, 50}.

1.6.5 Adsorption

An alternative method for the removal of heavy metal ions is adsorption, which is an effective and competitive process. Adsorption is the process of exchange of materials at the interface between two immiscible phases contacting each other. Adsorbent is a porous material with a high surface area and the ability to adsorb other substances by way of intermolecular forces onto its surface. The substance adsorbed or attached, is called adsorbate (e.g., metal ions, dye molecules etc.). Although certain phenomena associated with the adsorption process was known in ancient times, the uptake of gases by charcoal and clay was the first set of experiments carried out. In these cases, the interaction of H⁺ and metal ions between the solid and the surrounding aqueous solution is the main focus. Diffusion controlled mechanism of adsorption is presented in figure 1.3. Adsorption by porous adsorbents proceeds through three basic steps⁵¹.

- Transport of the adsorbate molecule from the bulk to the exterior of the adsorbent and adsorption on the exterior surface (External diffusion).
- Migration of the adsorbate into the pores of the adsorbent (Gradual adsorption stage).
- Interaction of the adsorbate with the available sites on the interior surfaces, binding with functional group onto the pore and capillary spaces of the adsorbent (Intra particle diffusion)

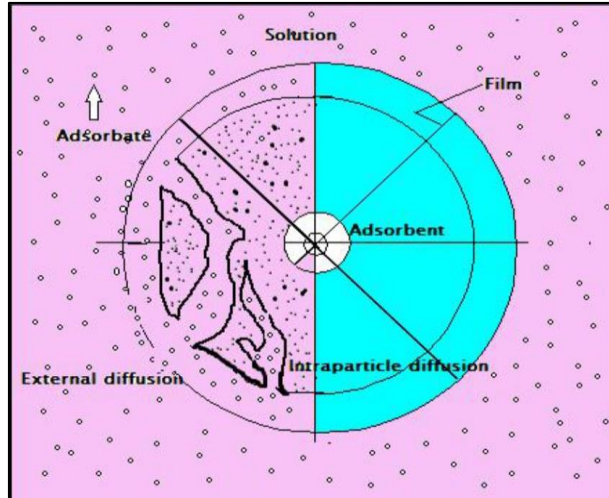
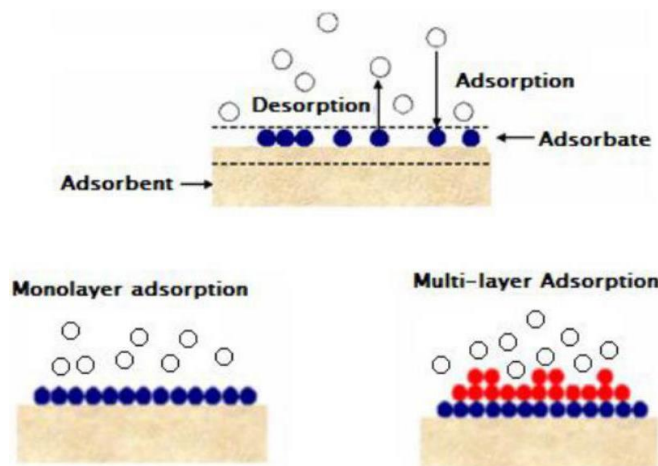


Figure 1.3 Adsorption Mechanism

Adsorption is widely used for various industrial applications and in water purification. The exact nature of bonding between the adsorbent and adsorbate depends upon the species involved during adsorption process. Adsorption Kinetics is defined as the rate at which substances are transferred from the liquid phase to solid phase.



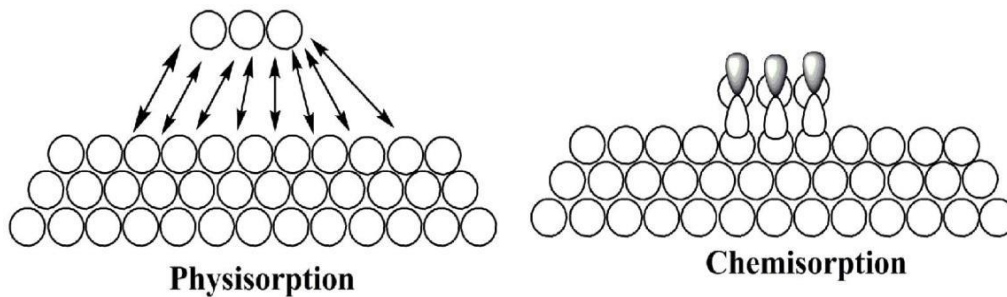
Adsorption results in a decrease of the residual forces, thereby resulting in decrease of surface energy, which in turn appears in the form of heat. The amount of heat evolved, when one mole of any adsorbate gas (or vapour) is adsorbed on a solid adsorbent⁵². The advantages of adsorption over other conventional treatment methods as per the literature available are as follows:

- Less land area (half to quarter of what is required in a biological system)
- Lower sensitivity to diurnal variation
- Greater flexibility in the design, operation and superior removal of organic contaminants.
- Fully Controlled Operation
- Scope for expansion & modular design Economical & Efficient method for TDS removal

Adsorption can be classified into two main categories depending upon the concentration, nature of the force existing between the sorbate and sorbent molecule and the nature and strength of adsorbent - adsorbate interactions.

In the adsorption process, the concentration of one substance is different at the surface of the other substance as compared to adjoining bulk or interior phase. It is further subdivided into

- Positive adsorption
- Negative adsorption



When the concentration of sorbate is more on the surface of adsorbent than in the bulk, it is called positive adsorption. It results in the transfer of solute to surface of the solid (in a solid- liquid system), where it accumulates until a dynamic equilibrium is reached with its concentration in solution. At this stage, the system is said to be in equilibrium and the ratio of solute concentration in the liquid and solid phases indicate the maximum extent of sorption possible under a set of experimental conditions. The variations of these experimental conditions can alter the position of equilibrium during the adsorption process. Such variations are expressed as adsorption isotherms⁵³.

When the concentration of the sorbate is less on the surface of the adsorbent than in the bulk, it is called negative adsorption. Dilute solutions of electrolytes, such as KCl, in contact with wood charcoal, exhibit this behavior. However, the same system registers a positive sorption at higher concentrations of the electrolyte⁵⁴.

Aqueous suspensions of finely divided solids exhibit charged solid surfaces. The origin of this charge may be either due to the interaction of functional groups on the solid surface with the aqueous medium (e.g. ion exchange) or due to the broken edges of micro crystallites constitutes the sorbent surface. Most adsorbent surfaces are heterogeneous and it is difficult to identify the individual types of sites and adsorbate interactions⁵⁵.

The broad categorization of the adsorption processes are:

- Physical adsorption
- Chemical adsorption

Physical adsorption or Van der Waal's adsorption is one in which the adsorbed molecules are held onto the surface of the adsorbent by weak physical or van der Waal's forces, similar to the condensation of a gas to form a liquid. Such adsorption is characterized by comparatively low heats of adsorption viz., 20-40 kcal/ mol. This kind of adsorption is reversible, since the molecules are not held strongly by the adsorbent.

Desorption (removal of adsorbed substance from the surface) processes are closely approximate to the adsorption curves as their mirror images, though the driving forces may be less. Forces responsible for physisorption are very weak. Multi-layer adsorption occurring as extended from one layer to another.

Chemical adsorption (chemisorption) or activated sorption takes place by covalent bonding. The union between the adsorbent and adsorbate is so firm that the product appears to be a surface compound. This type of adsorption involves interaction of free valencies at the surface of the adsorbent and adsorbate molecules. Complete interaction of all available valencies on the surface of the adsorbent would produce a monomolecular layer over the entire surface. In chemisorptions, the heat evolved (40-400 kcal/mol) is considerably higher than that evolved (20-40 kcal/mol) in physical adsorption.

Chemisorption is irreversible, since molecules are tightly held strongly by the adsorbent. The transition of physisorption to chemisorption may be possible, particularly at elevated temperatures, when the adsorbed molecules acquire sufficient energy to involve in chemical interaction with the sorbent surface⁵⁶.

A large number of materials have been extensively investigated as adsorbents for the removal of heavy metal ions. Some of the reported adsorbents include activated clay, zeolite, chitosan, silica gel, activated carbon, polymeric resin etc.

1.7 Review of Literature

1.7.1 Adsorption onto Natural Materials

Sorptive nature of sulphuric acid modified avocado seed (ASSA) was tested for toxic Cr^{6+} ions from water and wastewater by Bhaumik⁵⁷ *et al.*, where its equilibrium sorption capacity was observed as 333.33 mg/ g at 25°C.

Mun-Seon Song⁵⁸ *et al.*, registered the varied Ni^{2+} removal efficiency of modified clay at different pH environments with saturation time intervals, wherein the adsorption capacity of modified clay was 1.5 times larger than that of natural clay.

The sequestering capacity of *Raphia palm* fruit endocarp (nut) towards Pb^{2+} ions from aqueous solutions was studied by Abasi⁵⁹ *et al.*, where the particle size and temperature were reported to influence the sorption rate.

Ankit Balaria⁶⁰ *et al.*, investigated Pb^{2+} sorption by citrus peels containing the biopolymer pectin, suggested to possess a strong affinity for metal ions. FTIR spectra of the above system confirmed the involvement of carboxylic acid groups in binding of Pb^{2+} ions during the sorption process.

Biosorption of lead and cadmium ions by protonated *Sargassum glaucescens* biomass were carried out in a continuous packed bed column by Kazem Naddafi⁶¹ *et al.*, The selective sorption capacities of Pb^{2+} and Cd^{2+} at complete exhaustion point were determined to be 1.18 and 0.22 mmol/ g, respectively. Also, the regeneration efficiency of adsorbent by 0.1M HCl was achieved about 60 % and the maximum uptake capacity of Pb^{2+} by the regenerated biomass to be 0.75 mmol/ g.

Under optimized operational conditions, 78% and 94% sorption of Cd^{2+} and Pb^{2+} were achieved by Muhammad H. Al-Malack⁶² *et al.*, during the adsorption studies using activated carbon (AC) produced from municipal organic solid waste (MOSW).

Annadurai⁶³ *et al.*, observed the sorption characteristics of low-cost banana and orange peel wastes at 30°C for the uptake of Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , and Pb^{2+} ions in the concentration range of 5-25 mg/L. The sorption of preference was in the order $\text{Pb}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+}$ in case of both the adsorbents with increasing pH values, attaining a plateau at $\text{pH} > 7$, confirmed by the variations of zeta potential values.

Metal finishing wastewaters laden with specific divalent toxic ions were treated using natural (clinoptilolite) zeolites⁶⁴. The percentage adsorption and distribution coefficients were determined for the adsorption systems as a function of sorbate concentration.

Awan⁶⁵ *et al.*, studied the removal of Pb^{2+} , Cr^{6+} , Cu^{2+} and Zn^{2+} from their aqueous solutions employing ordinary sand where the phenomenon was illustrated on the basis of the interaction between the surface functional group of silicates (sand) and the metal ions.

Experimental verification of natural ponkan peel⁶⁶ as an efficient biosorbent for Pb^{2+} ions revealed a broad and intense sorption with a maximum at 3400 cm^{-1} assigned to O–H stretching group as evident from the EDX spectra.

Employability of MOL (Moringa oleifera leaves) in the removal of Pb^{2+} ions by Hari Kishore Kumar Reddy⁶⁷ *et al.*, was supported by specific characterization studies viz., FTIR, SEM and elemental analyses. Further studies with diluted HCl as desorbing medium, indicated the reusability of MOL as an efficient material.

Argun⁶⁸ *et al.*, stated the removal of Ni^{2+} ions from aqueous solutions using HCl modified pine tree bark and cone with the maximum removal efficiency 97% and 80% respectively at pH 8.

Martin-Dupont⁶⁹ *et al.*, have tested the sorption potential of coniferous barks for Cr^{3+} , Cu^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} ions. The maximum binding capacity followed the order of $\text{Cr}^{3+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$.

Trapping of Pb^{2+} ions using Robinia tree leaves⁷⁰ was verified through student's t-test and analysis of variances (ANOVA), the mathematical tools to describing functional relationship between dependent and independent variables.

Adsorption capacities of the stems, leaves and roots of *Quercus ilex* phytomass were compared for Cr^{6+} , Ni^{2+} , Cu^{2+} , Cd^{2+} and Pb^{2+} uptake at ambient temperature by Prasad⁷¹ *et al.*, thereby the metal uptake capacities were found to be in the order: $\text{Ni}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cr}^{6+}$ for root, $\text{Ni}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Cr}^{6+}$ for stem and $\text{Ni}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cr}^{6+}$ for leaf.

Aspen tree sawdust was examined by Hamed Mosavian⁷² *et al.*, for its potentiality to trap Cr^{6+} ions, the system was pH dependent and exhibited maximum adsorption at pH 2.0 at greater dose and prolonged agitation.

Effects of variations in parameters such as pH, contact time, adsorbent dose, initial Ni^{2+} concentration and particle size were emphasized in the selective Ni^{2+} adsorption by activated charcoal and non-conventional babhul bark⁷³.

Bingol⁷⁴ *et al.*, adopted batch process with *Nigella sativa* seeds (black cumin), a natural biosorbent to remove lead ions from aqueous solutions. Response Surface Methodology (RSM) and Artificial Neural Network (ANN) methodology were compared for their predictive capabilities in terms of the coefficient factor R^2 and root mean square error based on the validation data set to develop an approach for the evaluation of heavy metal biosorption process in this study.

The feasibility of coconut shell charcoal and its derived commercial activated carbon were investigated by Sandhya Babel⁷⁵ *et al.*, in the case of Cr^{6+} ions. Improvisation of their performances was ensured by surface modifications of the coconut shell charcoal and its commercial activated carbon with oxidizing agents such as sulfuric acid and nitric acid respectively.

1.7.2 Adsorption onto Animal Wastes

Dahbi⁷⁶ *et al.*, analyzed the sample of Cr^{6+} onto bone charcoal as a function of time, amount of charcoal, pH, concentration of Cr^{6+} sample volume and concluded that 90% removal efficiency at pH 1 was achieved for using 2 g of bone charcoal with the stirring time of 30 min.

Rapid removal of Cr^{6+} from aqueous solution by prawn shell activated carbon (PSAC) was established by Palvannan⁷⁷ *et al.*, the complex nature of PSAC characterized

using Scanning electron microscopy (SEM), Fourier Transform Infra-Red spectroscopy (FTIR) and X-Ray Diffraction (XRD) analyses. The maximum metal uptake was 100 mg/g under generalized conditions of 0.04 gram of PSAC dosage, 100 mg/L of Cr^{6+} at pH 2.

Chemically modified *Labeo rohita* Fish scales⁷⁸ was efficient in sequestration of Pb^{2+} under different experimental conditions. Sorption capacities (mg/g) of fish scales pretreated using bases were in the following order: $\text{Ca}(\text{OH})_2$ (200.76) > non treated (196.8) > $\text{Al}(\text{OH})_3$ (192.76) > NaOH (149.14). Gradation in sorption was observed at acidic pH 3.5.

The potential of pretreated crab and arca shell⁷⁹ discarded as waste materials from the fishing industry were converted into a biosorbent for Pb^{2+} and Cu^{2+} ions. The percentage removal was 40% within 60 min and later attained equilibrium after 4 h for both the systems.

1.7.3 Adsorption onto Industrial Wastes

Raziya Nadeem⁸⁰ *et al.*, evaluated the adsorption of Pb^{2+} using dried untreated and pretreated distillery sludge biomass which occurred rapidly within 30 min followed by slow controlled diffusion until the equilibrium was reached. The optimized parametric conditions were observed to be 24 h contact time, 100 mL volume of solution, 0.25 mm particle size and 0.5 g of loaded biomass.

Effective methylene blue removal from simulated wastewater using Indian Rosewood sawdust⁸¹, a timber industry waste proved its potential practices while pretreatment using formaldehyde and sulphuric acid. Percentage removals were directly proportional to dosages.

1.7.4 Adsorption onto Nanomaterials

Onundi⁸² *et al.*, have tested the effects of varying operating conditions on divalent metal ions removal using a novel nanosize composite as adsorbent. Characterization of the composite material showed the successful production of carbon nanotubes on granular carbon using 1% nickel nitrate as catalyst. The removal percentage at the equilibrium conditions varied for every metal, with Pb^{2+} recording 99 %, Cu^{2+} 61 % and Ni^{2+} 20 %.

Shihabudheen M. Maliyekkal⁸³ *et al.*, described that physisorption plays a dominant role for Pb^{2+} using nanoscale manganese oxide (NMO) and cellulose- NMO composite (C–NMOC). The performance of C– NMOC exceeded nanoscale-manganese oxide (NMO) prepared under similar conditions.