

Chapter I

Introduction

“The world can perform, act only with water”

-Thiruvalluvar

Water is considered to be the most abundant compound on earth, constituting about 70% of the planet's surface, being vital for all known forms of life¹. It is an essential and inevitable commodity for development and growth. Although two-thirds of the earth is covered by water, its chemical nature is one of the most important criteria that determines the usefulness for a specific need and as such not all the waters are fit for drinking; hence the problem of scarcity. On an average, a human being consumes about 2 litres of water everyday². 97% of water is found in oceans, large water bodies with 1.6% below ground in aquifers and 0.001% in air in the form of vapour, clouds and precipitation³. Also, 2.4% locked as glaciers and polar ice caps, with only 0.6% contributing towards lakes and ponds. The ‘dependency culture’ among the rural people has also been responsible for this state of affairs. The latest report indicates that about 15% of the total rural habitations of the country are facing water quality problems mainly due to excess of fluoride, arsenic, iron, nitrate contamination and salinity. India, being on the policy frame of drinking water has accorded the highest priority for rural drinking water. The government has realized that sustaining the system for the provision of safe water supplies has failed even after huge investments. Systems often fail due to poor operation and maintenance. This is due to the perception of the rural people that water is a social commodity to be provided free of cost by the government, rather than a scarce resource that should be managed by the community, through local level institutions, as an economic asset.

1.1 Importance of Water

Water plays an important role in the world economy, its need varying greatly from country to country, depending on climate and size of the population. The primary utility of water is for drinking and other domestic purposes apart from agriculture and irrigation⁴. Water consumption for this sector has consequently risen and is expected to linearly grow at a rate of 4.2% per year⁵. Industries and factories, a category that includes energy production use water for various purposes viz., cooling, processing, cleaning and removal of industrial wastes⁶.

Besides domestic, agricultural and industrial uses, water sources have been utilized for navigation, fishing and other recreational activities⁷.

1.2 Characteristics of Water

Potability of water is determined based on its characteristics⁸ as follows:

- ❖ Colorless, odorless and tasteless in nature
- ❖ Free from turbidity /suspended impurities /pathogenic/ microorganisms and anti-corrosive
- ❖ pH values between 6.5 and 8.0

1.3 Water Pollution and its Sources

Of all the problems faced due to environmental degradation, water pollution is the first and foremost menace gaining considerable attention. It is considered as the deterioration in the physical, chemical and biological properties of water brought about mainly by the presence of foreign materials through natural or anthropogenic sources leading to health hazards and a constant decline in the utility of water⁹. Even in the most unpolluted geographical areas, rain water with dissolved CO₂, O₂ and N₂ carry dust or other particulates in suspension picked up from the atmosphere. Mostly, water employed for industrial purposes reach water cycle, often being polluted by harmful chemicals and heavy metals, or else its temperature is raised effecting detrimental attributes in the water ecosystems. The root cause of water pollution may be attributed to many sources and types of pollutants¹⁰, which include

- ❖ Oxygen demanding wastes
- ❖ Disease causing agents
- ❖ Synthetic or organic compounds
- ❖ Plant nutrients
- ❖ Inorganic chemicals and minerals
- ❖ Sediments
- ❖ Radioactive substances
- ❖ Thermal discharges
- ❖ Oil

1.3.1 Oxygen Demanding Wastes

Dissolved oxygen is an essential requirement of aquatic life. Oxygen depletion caused by the demanding wastes comprise of sewage, paper mills, tanneries, food processing plants etc¹¹., Decrease in the dissolved oxygen (DO) content is an index of pollution.

1.3.2 Disease – Causing Agents

Water is a potential carrier of pathogenic micro-organisms which are the basic disease-causing agents. Pathogens enter water bodies through sewage and agro based industrial outlets.

According to an estimate nearly 2/3rd of all illness in India is related to water borne diseases such as Typhoid, Hepatitis, Jaundice, Cholera, Diarrhea and Dysentery¹².

1.3.3 Synthetic Organic Compounds

Discharges from the industries manufacturing fuels, plastics, pesticides, plasticizers, paints, fibers, detergents etc., imparts objectionable and offensive tastes, odours and colors to water streams even when they are present in low concentrations.

1.3.4 Plant Nutrients

Agricultural runoff and to some extent, municipal sewage forms the basis of enrichment of nutrients in water resources, apart from the natural biological process called eutrophication. Apart from sewage generation, organic wastes derived from milk, plants, tanneries, slaughter houses, paper mills, starch factories and fish processing plants impose the plant productivity of waters and extend algal growth in abundance termed as 'algal bloom'.

1.3.5 Inorganic Chemicals and Minerals

Inorganic salts, mineral acids, complexes of metals with organics in natural water and organo-metallic compounds, frame another source of pollution¹³. Also, pollution through Phosphates, Nitrates and Fluoride are alarming.

1.3.6 Sediments

In industrial areas heavy metals, plastics and other persistent organic compounds including pesticides are the major causes of soil pollution. The natural process of soil erosion gives rise to sediments in water. As a matter of rough estimate, suspended soil

loadings reaching natural waters are about 700 times as large as the one from sewage discharge. Sediments are suspended particles which are also important repositories for trace metals, eg: Cr, Cu, Bi, Mo, Co & Mn.

1.3.7 Radioactive Substances

Radioactive wastes are another special category of wastes that require special handling to protect the public. Because of the high levels of some dangerous pollutants that have accumulated in the environment, the very existence of mankind is in danger. The production of large quantities of 'Uranium Tailings' create the problem of radioactive pollution which is difficult to handle. Nuclear weapons testing in air, leakage from underground nuclear detorations etc. give rise to radioactive fallout. The discharge of radioactive wastes into the water systems is likely to create problems in the long run. There is a possibility that this may lead to oceanic pollution or pollution of underground water supplies. Water is also polluted by colloidal impurities such as emulsified oil, decomposed organic matter, finely divided clay and silica, organic waste products etc.

1.3.8 Thermal Discharges

Nuclear and thermal power stations use large quantities of water for cooling purposes. They discharge the resultant hot water often containing chemicals, into water streams. This results in increase in temperature of the water of the stream, which is injurious for fish and other aquatic organisms.

1.3.9 Oil

Pollution due to oil and petroleum products from refineries, drilling and pumping operations, shipyards and oil spills, have destroyed wild life and made water unfit for use. Many of the sea birds die¹⁴. Because their feathers get soaked with oil and they lose buoyancy and hence get drowned.

Table 1.1 The Common Water Pollutants and Their Adverse Effects

S. No.	Pollutants	Impact
1.	Organic Pollutants i) Oxygen Demanding wastes ii) Synthetic organic pollutants iii) Oil	Depletion of the DO endanger aquatic life, making water unfit for various uses, coating of oil spills cause reduction in light transmission and reflect in photosynthesis process
2.	Pathogens	Water borne disease such as cholera, typhoid etc.,
3.	Plant Nutrients	Affects aquatic life and causes groundwater pollution.
4.	Radioactive Pollutants	Toxic and accumulate in bones, teeth resulting in serious disorders.
5.	Suspended Solids and Sediments	Presence of suspended solids such as sludge and coal dust block the sunlight penetration in water retarding photosynthesis. Gills of fishes injured causing asphyxiation.
6.	Inorganic Pollutants	Aquatic flora and fauna also affected constituting public health problems.

1.4 Heavy Metal Pollution

Heavy metals are generally defined as environmentally stable elements of high specific gravity and atomic weight. The term ‘trace’ element is commonly used to describe substances which cannot be precisely defined but most frequently occur in the environment at lesser concentrations (mg/L)¹⁵.

Contamination of wastewaters with toxic heavy metal ions is a complex problem, due to an exponential increase in their use at industrial processes. Heavy metals present in nature entering water cycle through surface run-off and high way run-off also cause pollution¹⁶. Heavy metals present in solid wastes, municipal sewage sludges, land fill leachates pollute soils and percolate the ground water table. Higher concentrations of

heavy metals in water supplies are undesirable because of adverse effects on health¹⁷ due to environmental toxicity, corrosion of pipe works and also affecting the aesthetic equality of water. The most prevalent toxic metals are Pb, Cu, Cr, Cd and Ni.

1.4.1 Sources of Heavy Metal Pollution

Heavy metals find their way into the water cycle by

- ❖ Anthropogenic sources include either direct addition through industrial processing of ores and metals, leaching of metal from garbage and solid waste dumps, animals and human excretions, agricultural practices or through the atmospheric precipitation of industrial pollutants and automobile emissions¹⁸
- ❖ Natural processes, corrosion, geological weathering and volcanic activity
- ❖ Occupations where exposure to chromium and its compounds occur which comprise of anodizing, electroplating, stainless steel manufacturing, lithographing, textile processing, photography, welding, photoengraving, glass industry, copper etching and chrome tanning etc¹⁹.

The significant anthropogenic sources of heavy metal pollution are given in table 1.2.

Table 1.2 Significant Anthropogenic Sources of Heavy Metal Pollution²⁰

Industry	Metals	Sources of Pollution
Metalliferous Mining	Cd, Cu, Ni, Cr, Co, Zn	Acid mine drainage, tailings, slag heaps
Fertilizers	Cd, Cr, Mo, Pb, U, V, Zn	Run-off, surface and ground water contamination, plant bio accumulation
Manures, Sewage sludge	Zn, Cu, Ni, Pb, Cd, Cr, As, Hg	Land spreading threat to ground and surface Water
Alloys and steels	Pb, Mo, Ni, Cu, Cd, As, Te, U, Zn	Manufacture, disposal and recycling of metals. Tailings and slag heaps

Industry	Metals	Sources of Pollution
Landfill leachate	Zn, Cu, Cd, Pb, Ni, Cr, Hg	Landfill leachate, contamination of surface and groundwater
Electronics	Pb, Cd, Hg, Pt, Au, Cr, As, Ni, Mn	Aqueous and solid metallic waste from manufacturing and recycling process
Metal Finishing	Cr, Ni, Zn, Cu	Liquid effluents from plating processes
Batteries Paints and pigments	Pb, Sb, Zn, Cd, Ni, Hg Pb, Cr, As, Ti, Ba, Zn	Waste battery fluid, contamination of soil and groundwater Aqueous waste from manufacture, old paint deterioration and soil pollution

1.4.2 Toxicity of Heavy Metals

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. They may enter the human body through food, water, air or absorption through the skin. Industrial exposure accounts for a common route of entry into adults. Ingestion is the most common track of exposure into children. Children may develop toxic levels from the normal hand-to-mouth activity when they come in contact with contaminated soil. Heavy metal toxicity can result in damaged or reduced functioning of mental and central nervous system, damage to blood composition, lungs, kidneys, liver and other vital organs²¹. Allergies are common and repeated long-term contact with some metals or their compounds may even cause cancer.

All heavy metals are chalcophilic (affinity to sulphur) in their mineralogy and chemistry which is greater than that for oxygen. Hence they attack the sulphur bonds present in the enzymes and thus inhibit various metabolic activities of organisms. They also exert adverse effect by combining with one or more reactive groups essential for normal physiological functions²².

The modern age of heavy metal pollution has its beginning with industrial revolution. Arsenic and lead particularly make water dangerous to drink. Various regulatory bodies have set the maximum tolerant levels of these metals in potable water and industrial discharges. However, the metal ions are being added to the water system at a much higher concentrations than the maximum concentration limits (MCL'S), thus resulting in health hazards and environmental degradation.

1.4.3 Toxic Effects due to Metal Contamination

➤ Lead

Lead, a metal highly toxic in nature arises from a number of industrial and mining sources. Leaded gasoline is considered to be a major source of atmospheric and terrestrial lead, much of which eventually enter natural water systems. Except in isolated cases, it is probably not a major problem in drinking water since its permissible limit is 0.01 mg/ L, although the potential exists in cases, where the old lead pipes are still in use. Lead is also found in paint, dust soil and rarely in food. Children may be exposed to lead from lead printed toys and newsprint. Acute lead poisoning in humans causes severe dysfunction in kidneys, reproductive systems, liver, brain and the central nervous system. It is a well-known cumulative poison, found in the environment mostly because of mining and smelting, battery manufacturing and its use as an additive in fuel²³⁻²⁷.

➤ Nickel

Nickel is widely used in industries due to its resistance to corrosion, high strength over a wide range of temperature and good alloying properties. Its main sources include nickel-plating and alloy manufacture. It is also used as a catalyst in oil refining and other industrial processes. Other applications include power plants, gas turbine engines and cryogenic containers. The tolerance limit²⁸ of nickel in drinking water is 0.01 mg/L². Higher concentration causes cancer in lungs, nose and bones. Dermatitis (nickel itch) is the most frequent effect of exposure to nickel, as from use of coins and costume jewellery. Nickel carbonyl has been estimated as lethal to humans at atmospheric exposures of 30 mg/ L²⁹. Acute Ni(II) poisoning cause dizziness, headache, nausea, vomiting, chest pain, dry cough, shortness of breath, rapid respiration, cyanosis and extreme weakness³⁰.

➤ **Chromium**

Cr(VI) is extremely toxic to human beings and animals, even at 0.5 mg/L concentration. Continuous exposure by inhalation or skin contact causes perforation of nasal septum, asthma, dermatitis, dermal necrosis and may be fatal if swallowed, due to its strong oxidative potential. Approximate amounts of Cr(VI) in the form of effluents from electroplating, leather tanning, paint and pigment, glass, photography, ceramic, and textile dyeing industries are discharged into the natural bodies of water and land³¹⁻³⁵.

➤ **Iron**

Iron is continuously identified in municipal waste effluents, particularly in cities where iron and steel are manufactured.

The taste of iron in drinking water can be easily detected even at low concentrations of about 1.8mg/L. Hepatoma, a primary cancer of the liver, has become the most common cause of death among patients with hemochromatosis. This is an iron storage disease that results from the inability of the intestine to keep out unwanted iron³⁶.

➤ **Arsenic**

The leaching of arsenic into ground water may cause significant contamination. Arsenic being very toxic, occurs in natural waste and various industrial wastes, solids or liquids. High concentrations in drinking water are associated with endemic poisoning and the 'blank foot' disease³⁷. Arsenic compounds are absorbed through skin. It binds the globin of hemoglobin in erythrocytes. Arsenic toxicity creates vomiting diarrhoea, nausea, severe irritation of nose and throat, abdominal pain, skin eruptions, inflammations and sometimes even death³⁸.

➤ **Mercury**

Mercury is the most toxic inorganic pollutant available in natural waters due to the discharges from chlor alkali, paper and pulp, oil refining and battery manufacturing industries. The tolerance level of Hg(II) for discharge into inland surface waters and drinking water is 2 mg/L. Mercury affects central nervous system, chromosomes, pulmonary function and causes damage to kidneys^{39,40}. The biochemical kinetics of

mercury metalation in water under natural occurring conditions of pH and temperature has confirmed that inorganic mercury could be easily converted to more toxic organic mercury by certain microorganisms.

One very serious mercury pollution incident occurred in the 1950's at Minamata Bay, Japan where releases of mercury from a manufacturing plant into the Bay were ingested by fish. People eating the fish developed fatal neurological maladies. Infants and children were particularly vulnerable to this "Minamata Disease" which is caused by alkyl mercury poisoning⁴¹.

Methyl mercury in the water bio-magnified to higher levels from fishes to the local inhabitance through consumption. Methyl mercury concentrates in specific regions of the central nervous system and readily causes the blood- brain barrier as well as the placental barrier.

➤ **Cadmium**

Polluting sources of cadmium are mining, industrial operations and corrosion of galvanized pipes. The tolerance limit of cadmium in drinking water is 0.005 mg/L. It causes severe health hazards. Inclusive of enhancement of high blood pressure, kidney damage, destruction of red blood cells in humans⁴².

The symptoms of Itai-Itai disease was caused by chronic cadmium pollution amongst Japanese people. Poisoning in conjunction with other factors led to stresses of pregnancy and lactation, ageing and dietary deficiencies of vitamin D and calcium. The name arose from the cries of pain, "Itai-Itai" (ouch-ouch) by the most stricken victims, older Japanese women⁴³. Although men, young women and children were also exposed, 95% of the victims where post menopausal women over 50 years of age.

The disease started with symptoms similar to rheumatism, neuralgia orneuritis. Then came bone lesions, osteomalacia and osteoporosis along with renal disfunction. As escalated pain in the pelvic region caused the victims to walk with the duck like gait. Later even a slight strain caused bone fractures. The suffering lasted many years, before it finely ended to death.

➤ Copper

Copper is an essential element required for growth of plants, animals and humans. The human body normally requires copper at a level of about 1.4 to 2.1 mg for each kg of body weight. Trace amount of this metal is essential to life because it plays a major role in the enzyme function as a co-enzyme. The tolerance limit of copper in drinking water is 1.3 mg/L, beyond which considered to be toxic. Its deficiency is associated with anaemia, neutropenia, diarrhoea, demineralization of bone and Menkes syndrome⁴⁴. "Wilson's disease" occurs due to the excess deposition of copper in the lenticular nucleus of brain and liver. One manifestation of copper toxicity is cirrhosis of the liver in children (Indian Childhood Cirrhosis), which has been linked to boiling of milk in copper cookware⁴⁵.

Table 1.3 Heavy Metal – Industrial Effluents

Metal	Permissible Limit * (mg/L)
Arsenic	0.2
Chromium (VI)	0.1
Copper	3.0
Lead	0.1
Mercury	0.5
Iron	0.1
Nickel	3.0

***Standards References: WHO**

Table 1.4 Heavy Metal – Drinking Water

Permissible Limit (mg/L)			
Metals	Surface water* (mg/L)	Drinking water* (mg/L)	Fresh water* (mg/L)
Iron	(<30)	200	100
Copper	0.6	2000	6-30
Manganese	(<10)	50	10
Zinc	5	300	5
Silver	-	10	3-5
Arsenic	-	10	50
Cadmium	0.04	5	0.5-5
Mercury	0.002	1	0.2
Chromium	0.2	5	30
Nickel	0.5	20	10
Lead	0.5	10	20

*Standards References: APHA

1.5 Anionic Pollution

Presence of anionic species such as nitrate, nitrite, phosphate, chloride, sulphide and fluoride in water supplies may pose a serious environmental threat⁴⁶. They have been detected in surface and groundwaters and strict measures are being taken to minimize their concentrations and control their mobility in aqueous media. Primary anionic pollutants of water include phosphate, fluoride and nitrate.

1.5.1 Phosphate

Phosphorus is one among the 15th elements that are necessary for the plant growth. It is also the key component of Deoxyribo Nucleic Acid (DNA), teeth and bones. They occur naturally in rocks and other mineral deposits, and are formed when hydrogen

in phosphoric acid is replaced by various metals. Phosphates exist in three forms: orthophosphate, metaphosphate (or polyphosphate) and organically bound phosphate⁴⁷⁻⁴⁹. These forms occur in living and decaying plant / animal residues, as free ions or weakly bounded in aqueous systems.

❖ Sources

A large amount of phosphorus in receiving water bodies may come from different sources viz., natural sources (e.g. precipitation, decomposition of organic materials, soil erosion), artificial sources (chemical fertilizers, detergents, human and animal wastes), diffuse sources (e.g. run-off from agricultural fields) and point sources (sewage treatment sites). Orthophosphate is readily available to the biological community and typically found in very low concentrations in unpolluted waters. Poly forms are used for treating boiler waters and in detergents⁵⁰⁻⁵².

❖ Effects

Presence of phosphorus in natural waters in excessive amount is responsible for the eutrophication⁵³. Eutrophication is defined as the extraordinary growth of algae as a result of over enrichment of water bodies by nutrients, such as phosphorus and nitrogen. The two common symptoms of eutrophication are algal blooms and oxygen depletion. Thence, aquatic pollution due to high phosphorus concentration accelerates the development of phyto-plankton, algae and macro aquatic plants.

Decline of sub aquatic plants due to the formation of dead zones put the whole eco system at risk of disappearance. Not only it affects the aesthetic and ecological values, but also cause severe economic damages. According to Everglades hub (2013), a red tide⁵⁴ event had occurred near Hong Kong in 1998 affecting 90% of aquaculture farms and caused the estimated economic loss to 40 million USD. People's health may be at risk through consumption of poisonous fish and shellfish in eutrophication regions, leading to skin irritation, gastrointestinal illness, neurological damage and sometimes even death.

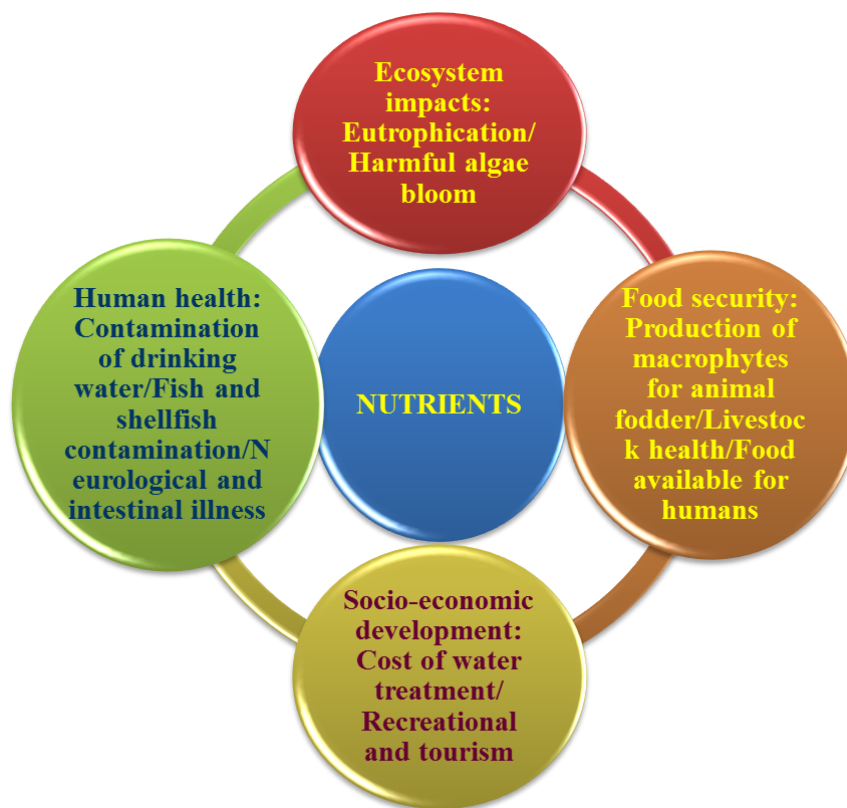


Figure 1.1 Impact of Excess Nutrients on Ecosystem

Obviously, as eutrophication has severe impacts on the environment and human well-being, the USEPA has recommended the acceptable level of total phosphorus in natural waters to be less than 0.05 mg/L⁵⁵.

1.5.2 Fluoride

The most commonly occurring mineral form of fluoride include fluorspar, cryolite and fluorapatite. The important inorganic fluorides are Hydrogen fluoride (HF), Calcium fluoride (CaF₂), Sodium fluoride (NaF), Fluorosilicic acid and Silico fluorides.

❖ Sources

The contaminants of fluoride, discharged into water bodies are from either natural geological sources or industries that use fluoride containing compounds as raw materials⁵⁶. The anthropogenic sources include coal burning, oil refining, steel production and phosphate fertilizer plants. The groundwater is more susceptible to fluoride accumulation because of its direct interaction with geological substrates underneath.

❖ **Effects**

Several researchers have reported that fluoride mainly produces effects on skeletal tissues of bones and teeth. When the concentration of fluoride is low, it gives protection against dental caries, especially in children. But when its concentration exceeds the permissible limit of 1mg/L in drinking water, it has an adverse effect on tooth enamel and may give rise to dental fluorosis. Elevated fluoride (3–6 mg of fluoride per litre) intakes leads to serious effects on skeletal tissues called skeletal fluorosis⁵⁷.

1.5.3 Nitrate

Nitrate is one of the most essential components of proteins and DNA in living organisms. Nitrogen is a major constituent of earth's atmosphere and occurs in many different forms like elemental nitrogen, nitrate, and ammonia. Nitrate and Nitrite anions are ubiquitous in the environment. Both species are produced by denitrification process⁵⁸ in which ammonia is oxidized by soil bacteria.

❖ **Sources**

Nitrate accumulation in the environment is mainly due to point sources and non-point sources. The rate of release of this pollutant depends on its concentration in the effluent or leachates, climatic conditions (rainfall), soil type and ground water table. The main sources⁵⁹ of nitrate pollution include:

- Run-off from land
- Sewage effluent
- Fertilizers and pesticides
- Animal feeds

❖ **Effects**

The regulation of nitrate in drinking water is primarily made essential because excess levels can cause methemoglobinemia or "blue baby" disease⁶⁰. Infants who consume vegetables rich in nitrates are more susceptible to the disease.

1.6 Treatment Methods of Heavy Metals

Technologies in the treatment of wastewater in terms of metal removal are divided into physical, chemical and biological process such as metal precipitation, ultra filtration, biological systems, oxidation, solvent extraction, electrolytic process, ion exchange, membrane filtration and adsorption.

1.6.1 Chemical Precipitation

Chemical precipitation processes involve the addition of chemical reagents, followed by the separation of the precipitated solids. Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers⁶¹.

1.6.2 Electro Dialysis

Electro Dialysis (ED) is a membrane process, during which ions are transported through semi permeable membrane, under the influence of an electric potential. The membranes are cation- or anion-selective, which basically means that either positive ions or negative ions will flow through^{62,63}. Cation-selective membranes are polyelectrolytes with negatively charged matter, which rejects negatively charged ions and allows positively charged ions to flow through and vice versa.

1.6.3 Coagulation/ Flocculation

Coagulation and flocculation are an essential part of drinking water treatment as well as wastewater treatment. Coagulation^{64,66,67} is the chemical reaction which occurs when a chemical or coagulant is added to water. The coagulant encourages the colloidal material in the water to join together into small aggregates called “flocs”⁶⁵. Suspended matter is then attracted to these flocs.

1.6.4 Ultrafiltration

Ultrafiltration is a separation process using membranes with pore sizes ranging between 0.1 to 0.001 micron. Typically, ultrafiltration will remove high molecular-weight substances, colloidal materials, organic and inorganic polymeric molecules. It is a pressure-driven purification process in which water and low molecular weight substances permeate a membrane while particles, colloids and macromolecules are retained.

The primary removal mechanism is size exclusion, although the electrical charge and surface chemistry of the particles or membrane may affect the purification efficiency^{68,69}.

1.6.5 Reverse Osmosis

Cellophane-like membranes separate pure water from contaminated water in reverse osmosis technique. This takes place when a pressure is applied to the concentrated side of the membrane, forcing purified water into the dilute side, the rejected impurities from the concentrated side being washed away in the reject water. Applications that have been reported for RO processes include the treatment of organics containing wastewater, wastewater from electroplating and metal finishing, pulp and paper, mining and petrochemical, textile, and food processing industries, radioactive and municipal wastewaters⁷⁰.

Table 1.5 Advantages /Disadvantages of Treatment Methodology

Methods	Advantages	Disadvantages
Oxidation	Rapid process for toxic pollutants removal	High energy costs and formation of by products
Ion exchange	Worthy removal of wide range of heavy metals	Adsorbents requires regeneration or disposal
Membrane filtration	Better removal of heavy metals	Concentrated sludge production and expensive
Adsorption	Flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants	Adsorbents require regeneration
Coagulation/ Flocculation	Economically feasible	High sludge production and formation of large particles
Electrochemical Treatment	Rapid process and effective for certain metal ions	High energy cost and formation of large particles
Ozonation	Applied in gaseous state, alternation of volume	Short half life
Biological Treatment	Feasible in removing some metals	Technology to be commercialized

1.6.6 Adsorption

Adsorption is one of the most popular and effective process for the removal of heavy metals and other ions from wastewaters. The adsorption process offers flexibility in design and operation and in many cases produce treated effluent suitable for reuse, free of colour and odour. In addition, as adsorption is a reversible process, regeneration of the adsorbent adds to the economy of the operation.

The steps involved in adsorption processes are (1) bulk solution transfer (2) film diffusion transfer (3) pore transport and (4) adsorption. Bulk solution transfer involves the movement of the material to be adsorbed through the bulk liquid to the boundary layer of fixed film of liquid surrounding the adsorbent. Film diffusion transport involves the transport by diffusion of the material to be adsorbed through the stagnant liquid film to the entrance of the pores of the adsorbent. Pore transport involves the transport of material to be adsorbed through the pores by a combination of molecular diffusion through the pore liquid and/or by diffusion along the surface of the adsorbent. Adsorption involves the attachment of the material to be adsorbed onto adsorbent at available adsorption sites⁷¹.

❖ **Role of Adsorbents: Activated Carbon**

Activated carbon has long been employed for the removal of pollutants and contaminants, mainly from aqueous media. They are known as very effective adsorbents due to their highly developed porosity, large surface area and high degree of surface activity. Its wide spread use is restricted due to high associated cost⁷². Few inexpensive adsorbents are broadly classified into five categories.

- ✓ **Natural minerals:** coal, peat, clays, perlite, red mud, hydrous ferric oxide, etc
- ✓ **Industrial wastes:** fly ash, bio gas slurry, chrome sludge, furnace slag etc
- ✓ **Agricultural wastes:** coconut shell, banana pith, orange peel, soya cake, olive cake, hazelnut shell, rice husk, sawdust, carbonized products
- ✓ **Forest wastes:** barks, leaves, carbonized products.
- ✓ **Aquatic plants:** weeds, algae, etc.

All these cost less materials have been employed as adsorbents with more economic value, facilitating industries to reduce the cost of waste recycling disposal and as a potential alternative to activated carbon.

1.7 Review of Literature

The potentiality of inexpensive materials either from natural sources or litters generated from other sectors viz., agro, marine, industrial by products, etc., (adsorbents) has familiarized as a novel alternative leading to better way in sequestering several heavy metal ions and anions from aqueous and industrial matrices. Some of the reported affordable materials as sorbents include: bark/tannin rich materials, lignin, chitin/ chitosan, modified wool, saw dust, rice bran, maize cob, corn husk, sugar cane bagasse, lemon peel, ground nut shell, almond shell, neem seed, papaya seed, egg shell, guava leaves, coir pith, fly ash, zeolites etc., Regeneration studies had also been performed to assess the reproducing ability of the materials to promote sustainability in wastewater treatments.

1.7.1 Agro based Materials

Materials from agricultural sources particularly those containing cellulose show potential sorption capacity for various pollutants. Agro based materials being chosen based on their eco- friendly nature and economically viable due to their unique chemical composition and especially available in copious amount.

Coconut husks litters frequently available in abundance with high tannin content in the husk promotes sorption of metals like Fe(III),Cu(II) and Pb(II) . Abdurasaq and Basiru⁷³ observed a significant influence in the sorption of all the aforesaid metals at pH 5 where the removal capacity was almost 90%. The sorption of Fe(III) and Cu(II) obeyed Freundlich isotherm with R^2 value equal to unity, implicating the iron adsorption due to chemical bonding; whilst Pb(II) showed better adsorption in Langmuir model.

Modified cashew nut shell exhibited potential sorption characteristics against Cu(II), Cd(II), Zn(II) and Ni(II) ions⁷⁴ with a maximum adsorption capacity of 407,437,456 and 457 mg/g creating monolayer adsorption with 100% removal of

Cu(II), the lower metal concentration recorded higher removal compared to high initial metal ion concentration due to the saturation sites of the nut shell.

Issabayeva et al.,⁷⁵ studied adsorption of Cu(II) onto activated carbon of palm shell which exhibit maximum sorption due to the activation employing complexing agents like boric acid and malonic acid at a maximum pH 5.

Vazquez et al.,⁷⁶ compared the sorption activity of chestnut shell pretreated by 4 % NaOH and acid formaldehyde wherein the former was found to be more effective in trapping Cd(II), Cu(II), Pb(II) and Zn(II) ions than its acid counterpart. Also, 100 mg/L of Cd(II) was sorbed preferentially against the other divalent ions.

Sorption ability of *Terminalia catappa* seed shell in the removal of Co(II) ions from aqueous solutions had been investigated by N Muthulakshmi Andal et al.,⁷⁷ The author compared the potentiality of the material by modification onto citric acid and HCl. Citric acid modified *Terminalia catappa* seed shell possessed greater adsorption capacity compared to HCl modification. Further probe of the study concentrated on the immobilization of the trapped Co(II) ions on the surface moieties of the selected sorbent material.

J. Sirajudeen et al.,⁷⁸ studied the removal efficiency of Cr(VI) using *Citrus limetta* (CL) peel through optimization of adsorption parameters viz., pH, contact time, initial concentration and adsorbent dosage.

Sreenivas et al.,⁷⁹ utilized ash gourd peel in the biosorption of Cr(VI) through column operations. Peel powder was characterized for particle size, specific area and other characteristics. The sorption capacity of the material was found to be 18.7mg/g.

Equilibrium studies for the sorption of Zn(II) and Cu(II) from aqueous solutions using sugar beet pulp and fly ash had been reported by E.Pehlivan et al.,⁸⁰ The study revealed the minimum influence of Na⁺ and Cl⁻ ions in metals' adsorption process.

The efficiency of HCl modified *Cucumis sativus* peel (CSP) in the removal of Cd(II) was revealed by Pandey et al.,⁸¹ where the required conditions of pH, adsorbent dosage, contact time and initial concentration were determined under Batch equilibration method. Maximum removal efficiency of 84.9% was registered for 20 mg/L Cd(II) ion at pH 5.

Njoku et al.,⁸² utilized sky fruit husk for the preparation of activated carbon chemically activated using ortho phosphoric acid. Batch studies were carried out in order to evaluate the potentiality of the prepared sorbent having BET surface area of 1211.57 m²/g for the anionic herbicide bentazon from aqueous solution.

A series of low cost agro-based materials viz., almond shell, ground nut shell, crushed coconut shell, *Tamarinds indica* seed and walnut shell were evaluated for Cr(VI) removal by Sanjeev Chaudri et al.,⁸³ Batch test signposted that Cr(VI) sorption followed the sequence: Tamarinds indica shell > Walnut shell > Almond shell > Ground nut shell > Crushed coconut shell.

Pb(II) / Cr(VI) - ANS(Areca nut shell) systems studied by Geetha et al.,⁸⁴ implied 86 % and 100 % removal of Pb(II) and Cr(VI) followed by a maximum desorption of 91% and 88% respectively.

1.7.2 Marine Species

Benavente Marthe⁸⁵ evaluated the adsorption of Cu(II), Zn(II), Hg(II) and As(V) by chitosan, of which enhanced As(V) removal occurred at pH 3, but for the other divalent ions between 4 and 6. Column studies revealed the breakthrough of Cu(II) and Zn(II) reaching iof about 60 and 30 bed volumes, respectively.

Biosorptive potential of cylindrical paper shell mussel (*Anodontoides ferussacianus*) had been investigated by Suleman Shahzad et al.,⁸⁶ in trapping toxic divalent metal ions, where they concluded multi-layer sorption.

Benliang Zhao et al.,⁸⁷ ascertained the characteristics of golden apple snail shell powder between pH 1.5 to 5.5 to adsorb Cd(II), where the Thermodynamic parameters indicated the process to be endothermic and spontaneous.

Biosorption behavior of Pb(II) and Cd(II) against blue green algae (*A.sphaerica*) had been reported by Azza M.Adel-Aty et al.,⁸⁸ FTIR results indicated that the amino, carboxyl, hydroxyl and carbonyl groups on the surface of the biomass were responsible for sorption. Mean free energy values calculated from D-R plot indicated chemisorption.

1.7.3 Plant Materials

Employment of bael leaves (*Aeglemarmelos corea*)⁸⁹ to sorb Pb(II) ions emphasized that the sorption had occurred within the walls of the hollow tubes of bael leaves, also carboxylic acid, thio ester and sulphonamide groups, being responsible for the process.

Results pertaining to sorptive action of activated carbon derived from agro forestry wastes onto Pb(II), Cu(II), Zn(II), Fe(II), Mn(II), Hg(II), Cr(II) and Ni(II) revealed that equilibrium adsorption data fitted best with Langmuir isotherm for Pb(II) uptake by Baobab shells⁹⁰.

Kinetic study of Pb(II)- *Eichhornia crassipes* roots⁹¹ sorption system implied that the data obeyed pseudo-second-order model with higher correlation coefficient R^2 value.

Bhattacharyya and Sharma⁹² developed an adsorbent from the mature leaves of neem (*Azadirachta indica*) tree for the removal of lead from wastewater, where the system supported maximum removal of 93% for an initial concentration of 100 mg/L. The adsorption was observed to be exothermic at ambient temperature.

Courtie Mahamadi et al.,⁹³ reported that water hyacinth fixed on calcium alginate beads to be viable metal enrichment media that can be used freely immersed in solution to achieve very high adsorption capacities and possible pre concentration of Ni(II) ions in aquatic environment .

1.7.4 Industrial By-products

Removal of cadmium and zinc from metal finishing industrial effluents using powder Activated carbon, granular Activated carbon and Fly ash was investigated by Basava Rao et al.,⁹⁴ where maximum uptake had occurred between 2.5 – 3 hours, invariably in case of industrial leachates employed at a dosage of 20 g/L.

Batch studies for Pb(II) removal from electroplating effluents using Sago waste was tested by Jeyanthi et al.,⁹⁵ the optimized conditions for enhanced sorption were pH 5, 3 hours contact time, 30°C temperature and 4 gm/L sorbent dose.

Removal of Ni(II) and Cr(VI) with bagasse fly ash and powdered activated carbon was examined by Rao et al.,⁹⁶ The laboratory results were extended to fit into Helfferich model in order to understand the mechanism of kinetics. A new constant was introduced in the study of the equation Helfferich, evidencing better fit of the model.

Reyam Naji Ajimi et al.,⁹⁷ probed the removal of divalent metal ions from industrial effluents waste plant. The maximum removal efficiency of Cr(II), Cd(II) and Pb(II) was achieved at pH 6 at optimum conditions.

Fly ash from a coal-fired power plant in the sorption of Zn(II) and Ni(II) from aqueous solutions had been investigated by Cetin S and Pehlivan E⁹⁸. Batch kinetic studies revealed that an equilibrium time of 1 hour was maintained for the sorption of divalent metal ions onto the sorbent.

Study on the sorptive ability of two different Turkish fly ashes⁹⁹ against Ni(II), Cu(II) and Zn(II) suggested the excess calcium content of the fly ash to be responsible for favorable metal binding.

1.7.5 Removal of Anions

Benyoucef and Amrani¹⁰⁰ observed that phosphate uptake by Aleppo pine was rapid indicating that the dominant mechanism might be chemisorption.

The zeta potential calculation and spectral analysis of phosphate removal using diethylenetriamine cross linked cotton stalk and wheat stalk¹⁰¹ revealed electrostatic attraction between phosphate ions and the later.

Krishnan and Haridas¹⁰² reported that ligand exchange was the principal mechanism involved in phosphate adsorption by iron impregnated coir pith and its precursor.

Maximum phosphorus adsorption on activated coir pith using sulphuric acid had been reported by Kumar et al.,¹⁰³ phosphorous investigation on phosphor uptake by modified egg revealed the process had occurred at high solution temperature, confirmed by positive ΔH^0 value.

Yue et al.,¹⁰⁴ concluded that the adsorption of phosphorus onto modified giant reed had occurred via physisorption.

Eberhardt et al.,¹⁰⁵ recorded the influence of Aspen wood on phosphate removal. Results suggested larger wood particles demonstrated better phosphate adsorption owing to the possession of higher number of carboxylate ions to complex ions.

Biswas et al.,¹⁰⁶ explored that foreign anions such as sulphates, chlorides and carbonates seldom registered any substantial influence on phosphate adsorption by La(III) loaded orange waste.

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