

Water, thou has no taste, no color, no odour; cannot be defined, art relished while ever mysterious. Not necessary to life, but rather life itself, thou fillest us with a gratification that exceeds the delight of the senses.

Water is one of the most indispensable resources and is the elixir of life. The importance of water can never been over emphasized. It exists in three states namely solid, liquid and gas. It is a unique substance, because it can naturally renew and clean itself, by allowing pollutants to settle out through the process of sedimentation. Water constitutes about 70% of the body weight of almost all living organisms¹. It acts as a media for both chemical and biochemical reactions and also as an internal and external medium for several organisms.

Earth is called the “blue planet” since 80% of its surface is covered by oceans and fresh water features. Life is not possible on this planet without water. It has been always been perceived as a gift from the gods as it rained from the heavens. In ancient culture, water was considered as a divine source and treated with devotion and worship. Even now humanity is in search of water in other planets to ascertain the existence of life. About 97.2% of water on earth is salty and only 2.8% is present as fresh water from which about 20% constitutes ground water. Ground water is highly valued because of certain properties not possessed by surface water². Fresh water is a renewable resource, yet the world’s supply of clean, fresh water is steadily decreasing. Biodiversity rich fresh water ecosystems are currently declining faster than marine or land ecosystems³.

1.1 Importance of water

Water is more important than food because lack of water will kill us faster than lack of food. Freshwater ecosystems are aquatic systems which contain potable water or water of almost no salt content. Fresh water resources include lakes and ponds, rivers and streams, reservoirs, wet lands and ground water. They provide the majority of our nation’s drinking

water resources, water resources for agriculture, industry, sanitation as well as food including fish and shellfish.

The health and well being of human race is closely tied up with quality of water used⁴. On an average, a human being consumes about 2 litres of water everyday and water accounts for about 70% of the weight of the human body. It is a remarkable solvent, where most elements and compounds can dissolve in its powerful molecular structure. Gases such as carbondioxide and oxygen can also dissolve in water making it readily available for photosynthetic and non-photosynthetic organisms to use⁵.

Ground water is used for domestic, agriculture and industrial purpose in most parts of the world. Everyday man requires 150 – 200 litres of water. The sources of water for irrigation in agriculture are rivers, lakes and small tanks. Domestic wastewater has always been a low cost option for farmers to go in for irrigation in water scarce regions of the world. Apart from its resource value, the high nutrient content of domestic wastewater helps farmers to fertilize their crops without spending substantial amounts on additional fertilizers.

India is endowed with a vast diversity of natural resources, water being one of them. Since agriculture is the back bone of the Indian economy, it receives the greater share of annual water allocation. About 92% of India's utilizable water is devoted to this sector, mostly in the form of irrigation⁶. Hydroelectric generation account for larger percentage of water demand from this sector. Nuclear and fossil fuelled power plants are applying staggering amounts of water for cooling purposes⁷. Most of the water used for industrial purposes is returned to water cycle, often being contaminated by chemicals and heavy metals or its temperature is increased leading to the detrimental effects in the water ecosystems.

Large amounts of water are also used in oil refineries, the steam turbine and heat exchanger systems⁸. According to the World Bank, demand for water in the power generation sector will raise from 67 to 228 billion m³ by 2025⁹. The demand for water is increasing exponentially due to progressive inclination in population, and the level of ground

water is facing declination considerably¹⁰. Industrial uses of water bodies vary from less than 5% of withdrawals in dozens of developing countries to as much as 85% in few developed countries. The proportion of water used for industrial purposes is often seen as an indicator of the economic development.^{11,12,13} Hence, with the increasing demand for water and its rising scarcity, the future demands of water for agriculture use cannot be met from fresh water resources alone.

1.2 Uses of water

Natural water systems comprise of chemical and physical processes that affect both the distribution and circulation of chemicals on the earth's surface. Water is required by industries for various reasons such as cooling, steam generation, heat exchange, gas scrubbing, washing of solids, surface rinsing etc. Since the plants and animals consumed by humans also depend on water, lack of it could cause both degradation and starvation. An average adult body contains 42 liters of water and with just a small loss of 2.7 liters he or she can suffer from degradation, displaying symptoms of irritability, fatigue, nervousness, dizziness, weakness, headaches and consequently reach a state of pathology. However, in present practices, water is being used and misused/abused in several activities without considering its cost involved in treatment and supply mechanism. These abuses are as follows:

- Washing and cleaning of vehicles and floors
- Irrigation of lawns, plants, kitchen gardens
- Flushing out wastewater
- Draining out water by leaving taps open and wasting water just because of ignorance and carelessness

1.3 Drinking water quality

In general, water is considered to be fit for drinking, only when it possesses certain characteristics¹⁴

- Should be colorless, odorless and tasteless in nature
- Should be free from turbidity and suspended impurities
- Should be free from pathogenic and micro organisms
- Should possess pH values between 7 and 8.5
- Hardness value should fall between 50 to 100 ppm
- Should be anti-corrosive and free from hazardous substances

1.4 Water pollution

Water pollution means the addition of any foreign material (organic, inorganic or radiological) to any water resource or any physical change in the natural water which may harmfully affect the life (human, agriculture or biological) ¹⁵. Water pollution is becoming a huge problem which is faced by all of us and as well as by every wild species. According to present scales for pollution of water, 10 to 15 billion pounds full of waste materials like garbage is thrown into seas and rivers of the entire world.

The water is polluted by sewage, industrial wastes and synthetic chemicals. The menace of water-borne diseases and epidemics still threaten the world population especially the developing and under developed countries. Today, the water is polluted with hundreds of toxins and impurities. This is a major problem in the global context. It has been suggested that it is the leading worldwide cause of deaths and diseases which accounts for the death of more than 14000 people daily.¹⁶ It occurs when pollutants are discharged directly into water bodies. The pathogenic organisms of these wastes are transmitted to the water and pose serious problems.¹⁷

The origin of these problems may be attributed to many sources and types of pollutants, which are broadly classified as¹⁸.

- (i) Organic pollutants
- (ii) Inorganic pollutants
- (iii) Suspended solids and sediments
- (iv) Radioactive materials
- (v) Heat

1.4.1 Organic pollutants

Organic pollutants may be further categorized as

- (i) Oxygen demanding wastes: These include domestic and animal sewage, biodegradable organic compounds and industrial wastes from food processing plants, paper and pulp mills and tanneries. These wastes undergo decomposition by bacterial activity in the presence of dissolved oxygen resulting in the rapid depletion of dissolved oxygen.
- (ii) Disease-causing wastes: These include pathogenic micro organisms, comprising mainly of viruses and bacteria, which can cause dangerous waterborne diseases such as cholera, typhoid, dysentery, polio and infectious hepatitis in humans.
- (iii) Synthetic Organic Compounds: These are man-made materials such as synthetic pesticides, detergents, pharmaceuticals, insecticides, paints, synthetic fibres and plastics. Most of these chemicals are potentially toxic to plants, animals and humans.
- (iv) Sewage and agricultural runoff: Sewage and runoff from agricultural lands supply plant nutrients aiding the growth of algae and aquatic weeds resulting in the degradation of the water body.

- (v) Oil: Oil spill may occur from tankers or during exploration. This results in the reduction of dissolved oxygen endangering sea life and birds. This does not allow light to pass through, reducing photosynthesis of marine plants.

1.4.2 Inorganic pollutant¹⁹

Inorganic pollutants comprise of mineral acids, inorganic salts, finely divided metals or metal compounds, trace elements, cyanides, sulphates and nitrates. Various metals and metallic compounds released from anthropogenic activities add up to water. The heavy metals are the most toxic among the trace elements. Heavy metals have great affinity for sulphur and attack the –SH bonds in enzymes. Carboxylic acid groups (-COOH) and amino groups (-NH₂) in protein may also be attacked by heavy metal ions. Water pollution by heavy metals occurs mostly due to street dust, domestic sewage and industrial effluents.

1.4.3 Suspended sediments and solids

Sediments are mostly contributed by soil erosion, natural processes, agricultural development, strip mining and construction activities. Suspended solids in water mainly comprise of silt, sand and minerals eroded from the land. Soil particles eroded by running water accumulate as silt in reservoirs, reducing their storage capacity. Apart from filling up reservoirs and harbours, they block the sunlight required for the photosynthesis of the bottom vegetation.

1.4.4 Radioactive materials

The radioactive pollutants may originate from the following anthropogenic activities such as mining and processing of ores (Uranium), increasing use of radioactive isotopes in research and also in agricultural, industrial and medical applications. Radioactive isotopes are toxic to life forms. For instance Sr⁹⁰, which emanates from the testing of nuclear weapons, accumulates in bone and teeth and causes serious disorders in human beings.

1.4.5 Heat

Waste heat is produced in all processes in which heat is converted to mechanical work. Considerable thermal pollution occurs from thermal power plants, where water is used as a coolant. The waste hot water released into the original water bodies reduces the dissolved oxygen content in the water.

1.5 Heavy metal pollution

Heavy metals are generally considered to be those whose density exceeds 5 g/cm^3 . At least 20 metals are classified as toxic and half of these are emitted into the environment possessing both beneficial and detrimental properties²⁰. Heavy metal ions have become an ecotoxicological hazard of prime interest and increasing significance, because of their accumulation in living organisms²¹. Heavy metal in the environment is of great concern due to their recalcitrance and consequent persistence²². Because of their toxicity, heavy metal pollution affect our ecosystem leading to possible health risks. In recent years, increasing awareness of water pollution and its far reaching effects has prompted concerted efforts towards the pollution abatement²³. The major sources of heavy metal contaminations are the discharges, industrial effluents into various water bodies.

Heavy metals have been identified as a common source of environmental pollution. The high affinity of heavy metals for soil organic matter has resulted in their accumulation in salts. The most disturbing fact about heavy metals and their speciation products is that they tend to end up in water sources where they accumulate by either physical and/or by biological processes in food chain of aquatic organisms.

According to public health surveys, large numbers of people have been exposed to the health hazards caused by heavy metals present in drinking water, surface water, ground water and animal tissue. The toxic effects of heavy metals are made more serious because of their non-biodegradable nature which makes heavy metal pollution a serious environmental

problem. Some of these metals are also known to attack the active sites of enzymes. They can be found in water, air and soil²⁴. The major sources of heavy metals in water and soil are wastewater streams of many industrial processes. Effluents from industrial processes such as electroplating, galvanization, mining, nuclear power operation, metallurgical operation, battery manufacturing, dye and pigment have been identified to contain high levels of heavy metals²⁵.

1.5.1 Sources of heavy metal pollution

Heavy metals find their way into the water cycle by anthropogenic sources which include either direct addition through industrial processing of ores and metals, use of metal and metal components, leaching of metal from garbage and solid waste dumps, animals and human excretions which contain heavy metals and agricultural practices or through the atmospheric precipitation of industrial pollutants and automobile emission²⁶. The significant anthropogenic sources of heavy metal ions are given in table 1.1

1.5.2 Toxicity of heavy metals

Heavy metal toxicity can result in reduced mental and central nervous function, lower energy levels and damages to blood composition, lungs, kidneys and other vital organs²⁷. Several heavy metals like chromium, manganese, cadmium, cobalt, copper, zinc, molybdenum, vanadium or iron are involved in catalytic functions relevant to living beings. However, they can be used by the microorganisms at very low concentrations (trace levels) (WHO/FAO/IAEA/1996), but the necessary balance has been effected by human activity, that has increased significantly the contributions to the natural environment of the metal ions²⁸. Elevated levels of heavy metals in water can be attributed to both natural and anthropogenic sources. Several disasters of metal poisoning episodes have been recorded from time, which have caused great ecological damage and led to the large number of human casualties.

The discharge of heavy metal into aquatic ecosystems has become a matter of concern over the last few decades. The presence of heavy metals in aquatic environment is known to cause severe damage to aquatic life, besides the fact that these metals kill microorganism during biological treatment of wastewater with a consequent delay of water purification process. Most of heavy metal salts are soluble in water and form aqueous solutions and consequently cannot be separated by ordinary physical means of separation. At higher doses, heavy metals can cause irreversible brain damage. Children may receive higher doses of metals from food than adults, since they consume more food for their body weight than adults.

All heavy metals are chalcophilic (affinity to sulphur) in their mineralogy and chemistry and this affinity towards sulphur is greater than that for oxygen. Hence, they attack the sulphur bonds present in the enzymes and thus inhibit various metabolic activities of the organisms. They also exert toxic effect by combining with one or more reactive groups essential for normal physiological functions¹⁸. Various regulatory bodies have set the maximum prescribed limits for the discharge of toxic heavy metals in the aquatic system (Table 1.2). However, the metal ions are being added to the water system at a much higher concentration than the prescribed limits by industrial activities, thus leading to health hazards and environmental degradation.

Table 1.1 Significant Anthropogenic sources of Heavy metal pollution²⁹

Industry	Metals	Sources of Pollution
Metalliferrous Mining	Cd, Cu, Ni, Cr, Co, Zn	Acid mine drainage, tailings, slag heaps
Agricultural Materials 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
Metallurgical Industries Alloys and Steels	Pb, Mo, Ni, Cu, Cd, As, Te, U, Zn	Manufacture, disposal and recycling of metals, tailings and slag heaps
Water Disposal Landfill leachate	Zn, Cu, Cd, Pd, Ni, Cr, Hg	Landfill leachate, contamination of ground and surface water
Electronics	Pb, Cd, Hg, Pt, Au, Cr, As, Ni, Mn	Aqueous and solid metallic waste from manufacturing and recycling processes
Metal Finishing Industry	Cr, Ni, Zn, Cu	Liquid effluents from plating processes
Miscellaneous Sources Batteries	Pb, Sb, Zn, Cd, Ni, Hg	Water battery fluid, contamination of soil and ground water
Paints and pigments	Pb, Cr, As, Ti, Ba, Zn	Aqueous waste from manufacture, old paint deteriorate and soil pollution

1.6 Heavy metals causing pollution

1.6.1 Nickel

Nickel is the 24th abundant element and it contributes about 0.008% of earth's crust. It occurs as sulphide and oxides deposits³⁰. It is widely used in industries due to its resistance to corrosion, high strength over a wide temperature range and good alloying properties. In addition, nickel has a good appearance. It is silvery white in colour and capable of taking high polish.

It is employed in nickel-plating, silver refining, acid mine drainage, steel and printing works, electronic devices, ceramics and coloured glasses. It plays a vital role in many processes of applied and fundamental sciences. During washing of the electroplating tanks, considerable amounts of the metal ions find their way into the effluents. Nickel is also used as a catalyst in oil refining and other industrial processes. The current applications of the metal include power plants, gas turbine engines, cryogenic containers and pollution abatement equipment. The tolerance limit of nickel in drinking water is 0.01 mg/L.³¹

It is an essential micro – nutrient for microorganisms and animals. It is associated with the synthesis of vitamin B₁₂ and its toxic effect includes dermatitis (Nickel – itch) and respiratory disorder. Dermatitis is found in women who use nickel containing jewellery particularly pierced earrings.³² Nickel carbonyl has been estimated as lethal to humans at atmospheric exposures of 30 ppm for 30 minutes.³³ Only 1 to 10% of dietary nickel ingested is found in tea, cocoa, peanuts and several other food stuffs. The tolerable daily intake of nickel is 300 to 600 mg/day.³⁴ Acute Ni(II) poisoning causes dizziness, headache, nausea and vomiting, chest pain, tightness of chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness.³⁵

Table 1.2 Permissible limits of various toxic metals

Metal contaminants	Drinking water requirement ³⁶ (mg/L) desirable limit	Industrial effluent discharge (mg/L) (Indian standards) ³⁷		Industrial effluents as per International standards (µg/L)	
		Inland Surface water	Into public sewers	WHO ³⁸	USEPA ³⁸
Nickel	0.10	3.00	3.00	2	-
Mercury	0.001	0.01	0.01	1	2
Arsenic	0.05	0.20	0.20	10	50
Cobalt	1.07	0.25	0.60	-	-
Lead	0.05	0.10	1.00	10	5
Chromium	0.05	0.10	2.00	50	100
Zinc	5.00	5.00	15.00	-	-
Copper	0.06	3.00	3.00	-	1300
Iron	2.00	0.01	0.01	-	-

1.6.2 Cobalt

It usually occurs in association with other metals such as copper, nickel, manganese and arsenic. It also exists as Co(II) and Co(III) which form a number of organic and inorganic salts. Cobalt is not found as a native metal but generally found in the form of ores. Cobalt is a ferromagnetic substance with a specific gravity and atomic weight of 8.9 and 58-93 g/mole respectively. It is a natural earth element present in trace amounts in soils, plants and in our diets. The average concentration of cobalt in soils throughout the world and in drinking water is 8 ppm and between 2-107 ppm respectively. The average daily intake of cobalt from food is estimated to be 5-40 mg/d. The average concentration of cobalt in

ambient air is approximately $0.0004\mu\text{g}/\text{m}^3$. Toxic effects on plants occur with cobalt concentration of 40 ppm.³⁹

Some natural sources of cobalt in the environment are soil, dust and sea water. It has also been used as a treatment for anaemia, because it stimulates the production of red blood corpuscles. Cobalt sulphide supported on alumina was found to have a potential use as a device trapping elemental sulphur over the temperature of 300-400°C.⁴⁰ People who live near hazardous waste sites containing cobalt may be exposed to higher level of this chemical. Acute exposure to high levels of cobalt by inhalation in humans and animals result in respiratory effects, such as a significant decrease in ventilatory function, congestion, edema and haemorrhage of the lungs.⁴¹

Vitamin B₁₂ is a cobalt containing compound that is essential for good health. It is also released from burning coal and oil and from car and truck exhausts. Cobalt and its salts are used in a variety of processings like preparation of magnetic, wear resistant super alloys which maintain their strength at high temperatures, as paint drier, a ground coat for porcelain enameling used on steel bathroom fixtures and large appliances and as an ingredient of coloured pigments. Cobalt blue gives a distinct deep blue colour to glass, ceramics, inks, paints and varnishes.

Other effects include cardiac effects such as functional effects on the ventricles and enlargement of the heart, congestion of the liver, kidneys and immunological effects that include cobalt sensitization which can precipitate an asthmatic attack in sensitized individuals.⁴² Cardiovascular effects were observed in people consuming large amounts of beer over several years which contain cobalt sulphate as a foam stabilizer. The effects are characterized by radiogenic shock, sinus, tachycardia, left ventricle failure and enlarged hearts. The beer drinkers ingest cobalt at an average concentration of 0.04 mg per kg per day. Health impairments may also be caused by radiation of radioactive cobalt isotopes.⁴³ This can cause sterility, hair loss, vomiting, bleeding, diarrhea and coma. Gastrointestinal effects

on the blood, liver injury and allergic dermatitis have also been reported in humans due to cobalt oral exposure. Powdered cobalt in metal form is a fire hazard.

1.6.3 Iron

Iron is the fourth most abundant element which constitutes about 5 % of the earth's crust. Most of the iron in the crust is found combined with oxygen as iron oxide minerals (haematite and magnetite). It exists in two forms, soluble ferrous iron (Fe^{2+}) and insoluble ferric particulate iron (Fe^{3+}). Iron is released to the environment from anthropogenic activities that include industries like iron and steel, dyeing, pigment, fertilizer, chloralkali, oil refining, wood preservative and rubber⁴⁴.

The presence of iron in natural water may be attributed to the dissolution of rocks and minerals, acid mine drainage, landfill leachate sewage or engineering industries. Iron in water is generally present in the ferric state. The concentration of iron in well aerated water is seldom high but under reducing conditions, high concentrations of soluble ferrous iron may be found, which may exist in some ground water, lakes or reservoirs.

Iron is an essential element in human nutrition. Iron is needed in the diet to maintain good health. Most of the iron in our body is contained in red blood cells as hemoglobin. Lack of iron can cause anemia but excessive iron is toxic. Large amounts of ingested iron can cause excessive levels of iron in the blood which can react with peroxides to produce free radicals. These are highly reactive and can damage DNA, proteins, lipids, and other cellular components. Thus, iron toxicity occurs when there is free iron in the cell, which is due to the iron levels exceeding the capacity of transferrin to bind the iron⁴⁵.

Haemochromatosis is the most common form of iron overload disease. Healthy people usually absorb about 10 % of the iron contained in the food they eat, which meets normal dietary requirements. People with haemochromatosis absorb upto 30 % of iron. Over time, they absorb and retain between five to twenty times more iron than the body needs. The extra iron building

up in the body damages the liver, heart, pancreas and endocrine glands⁴⁶. Haemochromatosis leads to serious problems such as arthritis, damage to the pancreas, heart abnormalities and thyroid deficiency⁴⁷.

The presence of iron at concentrations above 0.1mg/L will damage the gills of the fish. The free radicals are extremely reactive and short lived. The free radicals formed by the iron on the surface of the gills will cause oxidation of the surrounding tissue and this will lead to massive destruction of gill tissue and cause anemia. The presence of iron in drinking water supplies is objectionable for a number of reasons. Under the pH condition existing in drinking water supply, ferrous sulphate is unstable and precipitates as insoluble ferric hydroxide, which settles out as a rust coloured silt. Such water, often tastes unpalatable even at low concentration (0.3 mg/L) and stains laundry and plumbing fixtures. The Dietary Reference Intake (DRI) lists the Tolerable Upper Intake Level (TUL) for adults as 45 mg/day. For children under fourteen years old, the TUL is 40 mg/day⁴⁸

1.6.4 Lead

Lead is the most ancient industrial poison known to man. In nature, it mainly occurs as Galena (PbS) and it constitutes about 15 ppm of the earths' crust³⁶. Lead is the most widely used metal after iron. Apart from natural weathering processes, industries such as battery manufacturing, printing and pigment, metal plating and finishing, ammunition, ceramic and glass generate large quantities of wastewater contaminated with lead. In drinking water, lead contamination occurs due to the corrosion and leaching of lead pipes and Pb/Sn solder joints associated with copper service lines used in household plumbing⁴⁹.

Lead, a metal highly toxic in nature arises from a number of industrial and mining sources. Leaded gasoline is observed to be a major source of atmospheric and terrestrial lead, much of which eventually enter natural water systems. Except in isolated cases, lead is probably not a major problem in drinking water although the potential exists in cases where

the old lead pipe is still in use. Lead is also found in paint, dust soil, drinking water and rarely in food. Children may be exposed to lead from lead printed toys and newsprint.

Acute lead poisoning in human causes severe dysfunction in the kidneys, reproductive system, liver, brain and the central nervous system. Lead 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 fuel.⁵⁰ Organic tetra ethyl lead is about 10 to 100 times more toxic than inorganic lead due its rapid lipid solubility nature. Tetra ethyl lead is absorbed by inhalation of volatile compound or by its dermal entry into the body causing damage to the central nervous system³⁶. The tolerable daily intake of lead is about 300 to 350 $\mu\text{g}/\text{day}$ ⁵¹.

1.6.5 Chromium

Chromium is the 21st most abundant element in the earth's crust with an average concentration of 100 ppm⁵². Chromite is the important ore of chromium which contains about 68 % chromium oxide and 32 % iron oxide. Chromium compounds are found in the environment, due to the erosion of chromium containing rocks and can be distributed by volcanic eruptions. Industries such as electroplating, leather tanning, cement preservations, textiles, steel, canning, plating, paints and pigments, discharge Cr(VI) into the water⁵³.

Humans are exposed to chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The levels of chromium in air and water are generally low⁵⁴. Contaminated well water may contain the dangerous Cr(VI); hexavalent chromium. The main route of chromium uptake, as Cr(III) occurs in most people eating many vegetables, fruits, meats, yeast and grains, that contain Cr(III). Various ways of food preparation and storage may alter the chromium contents of food, as in the case of food stored in steel tanks or cans leading to enhanced chromium concentrations.

Cr(VI) is danger to human health, mainly for people who work in steel and textile industry. It is known to cause various detrimental health effects. When it is a compound in leather products, it can cause allergic reactions, such as skin rashes. Inhaling Cr(VI) can cause nose irritations and nose bleeds. Cr(VI) moves readily through soils and aquatic environments and is better absorbed than Cr(III). Hexavalent chromium is found to be more toxic than trivalent chromium. Absorbed Cr(VI) readily passes through the membrane of red blood cells and bound to the globin fraction of the haemoglobin⁵⁵.

Other health problems that are caused by Cr(VI) are respiratory problems, weakened immune system, kidney and liver damage, alteration of genetic material, lung cancer and death. The health hazards associated with exposure to chromium are dependent on its oxidation state. With the metal form being in low toxicity, the hexavalent form is more toxic. The adverse effects of hexavalent form on the skin may include ulcerations, dermatitis and allergic skin reactions. Respiratory symptoms may include coughing and wheezing, shortness of breath and nasal itch.

1.6.6 Cadmium

Cadmium is recognized as one of the toxic metals and it often occurs together with zinc in nature as sulphide deposits. The igneous rock contains 0.03 ppm cadmium on an average. Polluting sources of cadmium are mining, industrial operations and corrosion of galvanized pipes. Dumping of this metal into rivers is harmful to fish and plants. The tolerance limit of cadmium in drinking water is 0.005 mg/L. It causes severe health hazards. There is evidence that trace pollutants of the metal might enhance high blood pressure, kidney damage and destruction of red blood cells in human.

The symptoms of Itai-Itai disease⁵⁶ was caused due to chronic cadmium. It is named for the severe pains caused in the joints and spine leading to softening of bones and kidney failure due to acute cadmium poisoning. The name arose from the cries of pain, “Itai-Itai” (ouch-ouch) by the most stricken victims, older Japanese women. The Japanese Smelting

mining company discharged cadmium into the waste water, as they mined 3,000 tons of zinc-lead ore per day. Downstream farmers withdrew the fine particles of floatation tailings in the Jinzu river along with water for drinking and irrigation purposes⁵⁷. The nearby localities which had lived more than thirty years within three kilometers of the lower stream of Jinzu river developed Itai Itai. Although men, young women and children were also exposed, 95% of the victims were post menopausal women over 50 years of age. The disease started with symptoms similar to rheumatism, neuralgia or neuritis. 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 could last many years before it finely ended with death.

1.6.7 Copper

Copper and its compounds have been used by man since prehistoric times. It was the first metal harnessed by man and it ranks second in its usefulness to the human race. The source of copper include windblown dusts, volcanic emissions and the rest from anthropogenic sources including metal production, wood and fossil fuel combustion and waste incineration. The concentration of copper in soil ranges between 2 and 100 ppm with a man value of 20 ppm. In unpolluted wares, copper concentrations have been estimated at 0.0006 to 0.4 ppm. Copper is an essential element for plants, animals and humans and is a component of many metallo-enzymes and respiratory pigments. Approximately, 40 to 70% of the orally ingested copper is retained; the rest is eliminated through the bile, faeces and urine.⁵⁸

In human beings, the acute chronic manifestations of copper poisoning are dependent on the mode of contact of surroundings in which this contact occurs. An allergic contact dermatitis⁵⁹ may result from direct exposure to copper salts. The other effects include pharynx, metal fume fever, stuffiness of the head, nausea, vomiting, diarrhea, jaundice and extensive liver damage.

1.6.8 Zinc

Zinc is one amongst the ubiquitous elements; its mean concentration in the earth's crust is estimated as 70 ppm. The sources of zinc pollution are natural as well as anthropogenic. The natural sources involve wood combustion and waste incineration. The major share of the total world's production of zinc is used up in industrial applications such as zinc coating to protect iron and steel by hot dip galvanizing, electro galvanizing, spraying, painting etc.^{60,61} It is essential for functioning, of various enzyme systems in human and participates in protein and carbohydrate metabolism of animals. The recommended human daily intake of zinc is reported to be within a range of 3.2 – 29 mg. Symptoms of zinc toxicity include vomiting, dehydration, stomach pain, nausea, lethargy, dizziness and muscle in coordination. Zinc salts particularly zinc chloride produce dermatitis upon contact with skin. Zinc stearates have been found to be the possible cause of pneumonitis.

Zinc compounds can produce irritation and corrosion of the gastrointestinal tract, along with acute renal tubular necrosis and interstitial nephritis. Inhalation of high concentrations of zinc chloride from smoke bombs detonated in closed spaces may cause chemical pneumonitis and adult respiratory distress syndrome. In the occupational setting, inhalation of fumes from zinc oxide is the most common cause of metal fume fever⁵².

1.6.9 Arsenic

Arsenic is a toxic element that can be found in various industrial wastes. The leaching out of arsenic into ground water may cause significant contamination. Its compounds have been used as insecticides eg: lead arsenate and also herbicides. It is highly generated from fossil fuel burning. Fertilizer plant liquid effluents are reported to contain the element ranging from 0.27-3.2 mg/L. The high concentrations of this element have been reported in drinking water and are associated with endemic poisoning and the blank foot's disease. The blood contains about 25 mg of arsenic. It gets easily adsorbed through stain. It binds globin of haemoglobin in erythrocytes. Chronic poisoning by arsenic toxicity results in vomiting,

diarrhea, nausea, severe irritation of nose and throat, abdominal pain and loss of hair and even death. The toxicity of arsenic in +3 state is higher than that of arsenic in +5 state since arsenite reacts with sulfhydryl group while arsenate does not. Arsenates are known to stimulate the growth of plants however excessive amount of arsenic in irrigation reduce the yield of crops. It is a metabolic inhibitor and causes iron deficiency.⁶²

1.6.10 Mercury

Mercury is generally considered to be one of the most toxic metals found in the environment. Once mercury enters the food chain, progressively larger accumulation of mercury compounds takes place in human and animals. The major sources of mercury pollution in environment are industries like chlor-alkali, paints, pulp and paper, oil refining, rubber processing and fertilizer, batteries, thermometers, fluorescent light tubes and high intensity street lamps, pesticides, cosmetics and pharmaceuticals.^{60,61} Mercury brings about genetic defects causing chromosome breaking and interference in cell division, resulting in abnormal distribution of chromosome, impairment of pulmonary function and kidney, chest pain and dyspnoea. Methyl mercury causes deformities in the offspring, mainly affecting the nervous system (teratogenic effects). Children suffer from mental retardation, cerebral palsy and convulsions. The harmful effect of methyl mercury on aquatic life and humans was amply brought out by the Minamata episode in Japan.⁶³

1.7 Physico-Chemical Treatment Techniques

Different treatment techniques for wastewater laden with heavy metals have been developed in recent years to improve the quality of the effluent. Although various treatments such as chemical precipitation, coagulation-flocculation, ion exchange and membrane filtration can be employed to remove heavy metals from contaminated wastewater, they have their inherent advantages and limitations in applications.

1.7.1 Chemical precipitation

Chemical precipitation is widely used for heavy metal removal from inorganic effluents. This method involves the precipitation of heavy metal as their hydroxides using lime⁶⁴. Lime is generally favoured for precipitation purposes due to its low cost, ease of pH control in the range 8 to 10 and the presence of excess of lime also serves as an adsorbent for the removal of metal ions. Lime precipitation was employed by Chareerntanyarak⁶⁵ for the removal of Zn(II), Cd(II) and Mn(II) ions.

Papadopoulos et al.,⁶⁶ investigated the removal of Ni(II) from a metal finishing industrial effluent. The advantages of lime precipitation are simplicity of the process, inexpensive equipment requirement, convenient and safe operation. The disadvantages are excessive sludge production, increasing cost of sludge disposal, slow metal precipitation and poor settling⁶⁷.

1.7.2 Coagulation-flocculation

The coagulation process destabilizes colloidal particles by adding a coagulant and results in sedimentation. To increase the particle size, coagulation is followed by the flocculation of the unstable particles into bulky flocs. This technique includes pH adjustment and involves the addition of ferric/alum salts as the coagulant to overcome the repulsive forces between particles⁶⁸. Li et al.,⁶⁹ used sodium diethyl-dithiocarbamate as a trapping agent and both poly-ferric sulphate and poly acrylamide as the flocculants to treat copper containing electroplating wastewater. The advantages of lime based coagulation are fast sludge settling, dewatering characteristics, bacterial inactivation and sludge stability⁷⁰. The process has limitations such as high operational cost due to chemical consumption and increased volume of sludge generation.⁷¹

1.7.3 Membrane filtration

This method is used to remove suspended solids, organic compounds and inorganic contaminants such as heavy metals. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultrafiltration, nanofiltration and reverse osmosis can be employed for heavy metal removal.

1.7.3.1 Ultrafiltration

This utilizes permeable membrane to separate heavy metals, macromolecules and suspended solids from inorganic solution on the basis of pore size (5-20 nm) and molecular weight of the separating compounds (1000-100,000 Da). This enables ultrafiltration to allow the passage of water and low molecular solutes, while retaining the macromolecules, which have a size larger than the pore size of the membrane⁷². Yurlova et al.,⁷³ explored the removal of Ni(II) ions from a synthetic solution using micellar-enhanced ultrafiltration.

Ultrafiltration presents some advantages such as lower driving force and smaller space requirements due to its high packing density. However, the performance of the membrane was decreased due to membrane fouling, which in turn results in high operation costs for the membrane system⁷⁴.

1.7.3.2 Nanofiltration

The separation mechanism involves steric (sieving) and electrical effects. A potential is created between the charged anions in the nanofiltration membrane and the co-ions in the effluent to reject the latter. The significance of this membrane depend on its small pore and membrane surface charge, which allows charged solutes smaller than the membrane pores to be rejected along with the bigger neutral solutes and salts⁷⁵. Ahn et al.,⁷⁶ investigated the removal of Ni(II) ions from electroplating wastewater using polyvinyl alcohol as the skin materials of NTR 7250 membrane. They found that Ni(II) removal was dependent on applied pressure and initial metal concentrations. Depending on the membrane

characteristics, nanofiltration can remove metal at a wide pH range of 3-8 and pressure 3-4 bar. Nanofiltration process requires lower pressure which results in lower treatment costs. However, the cost and life span of the membrane is not met within the expectations.

1.7.3.3 Reverse osmosis (RO)

This is a pressure driven membrane process, where water can pass through the membrane, while the heavy metal is retained. The removal performance of an ultra-low pressure reverse osmosis membrane with polyamide as the skin material was investigated for the separation of Cu(II) and Ni(II) ions from both synthetic and real plating wastewater⁷⁷. Using polyamide as the same skin material for the membrane, Qin et al.,⁷⁸ also employed RO for the treatment of nickel contaminated wastewater directly discharged from a metal plating industry.

The added advantages of using RO are chemical stability, mechanical strength and ability to withstand high temperature. In spite of its benefits, RO has some limitations. Due to the suspended solids / oxidized compounds such as chlorine oxides, small pores are developed on the membrane making it more prone to fouling. Cations such as Cd(II) and Cu(II) present in the contaminated wastewater promote membrane fouling. The replacement of the membrane increases the operational costs. Other drawbacks are the high energy consumption, since pressure is the major parameter which is required for the heavy metal removal⁷⁹.

1.7.4 Ion exchange

Ion exchange, a reversible interchange of ions between the solid and liquid phases, where an insoluble substance (resin) removes ions from an electrolytic solution and releases other ions of like charge in a chemically equivalent amount without any structural change of resin.

Synthetic resins such as INR 77 and SKN 1 were employed to investigate the total uptake of Cr(III) from synthetic solution by Rengaraj et al.,⁸⁰. Other resins such as 1200H,

1500H and IRN97H were also employed to study the kinetics of Cr(VI) uptake from real and synthetic wastewater⁸¹. Chiarle et al.,⁸² used Duolite GT-73 a chelating synthetic resin to adsorb Hg(II) from water.

Unlike chemical precipitation, ion exchange does not present any sludge disposal problems. Since the equipment is portable, it is convenient for field work. The experiment can be done quickly and results are reliable. The main drawbacks are, suitable ion exchange resins are not available for all heavy metals, the capital and operational costs are high⁸³.

1.7.5 Electrochemical treatment techniques

1.7.5.1 Electrochemical precipitation

In electrochemical precipitation, electrical potential is utilized to modify the conventional chemical precipitation to maximize the removal of heavy metals from contaminated wastewaters. Electrochemical precipitation was employed for the removal of Cr(VI) from electroplating wastewater⁸⁴. Grebenyuk et al.,⁸⁵ reported that heavy metal can be carried over through electrochemical oxidation/reduction processes in an electrochemical cell without a continuous feeding of redox chemicals, thus avoiding space, time and energy consumption.

1.7.5.2 Electrodialysis

Electrodialysis is a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying electrical potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cations towards the cathode, crossing the anion exchange and cation exchange membranes⁸⁶. Tzanetakis et al.,⁸⁷ evaluated the performance of the ion exchange membranes for the electrodialysis of Ni(II) and Co(II) ions from a synthetic solution.

Electrodialysis offers advantages for the treatment of wastewater laden with heavy metals as it has the ability to produce a highly concentrated stream for recovery and the rejection of undesirable impurities from water. Moreover, valuable metals such as chromium and copper can be recovered. Since ED is a membrane process it requires clean feed, careful operation, periodic maintenance to prevent any damages to the stack.⁸⁸

1.7.5.3 Membrane Electrolysis

Membrane electrolysis, a chemical process driven by an electrolytic potential, can also be applied to remove metallic impurities from metal finishing industrial wastewater. There are two types of cathodes used: a conventional metal cathode and a high surface area cathode. When an electrical potential is applied across an ion exchange membrane, reduction–oxidation reaction takes place in electrodes⁸⁹.

The feasibility of electrochemical Cr(VI) removal from synthetic wastewater using carbon electrodes was investigated. More than 98 % of Cr(VI) removal with an initial metal concentration of 8 mg/L could be achieved at pH 2.0⁹⁰. The major drawback of membrane electrolysis is its high energy consumption.

1.8 Adsorption - A Promising Method

Amongst all the treatment process mentioned, adsorption is one of the most popular and effective process for the removal of heavy metals from wastewater. The adsorption process offers flexibility in design and operation and in many cases produces 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. Adsorption is the process of accumulating substances that are in solution on a suitable interface. It is a surface phenomenon, which involves a mass transfer operation, in that a constituent in the liquid phase is transferred to the solid phase. Adsorbate is the substance

that is removed from the liquid phase at the interface and adsorbent is the solid phase onto which the adsorbate accumulates.

The adsorption process takes place in different steps (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 sites⁹¹.

1.8.1 Treated Low cost Adsorbents

Activated carbon has long been studied as an adsorbent for the removal of pollutants and contaminants, mainly in aqueous media. They are known as very effective adsorbents due to their highly developed porosity, large surface area, variable characteristics of surface chemistry and high degree of surface activity. Even though commercial activated carbon is a preferred adsorbent for the removal of micro pollutants from the aqueous phase, its wide spread use is restricted due to high associated costs. In recent years, the search for low cost adsorbents that have metal binding capacities has intensified. Currently, there are many studies on the development of low-cost adsorbents and these can be broadly classified into five categories.

1. Natural minerals and similar materials like coal, peat, clays, perlite, red mud, hydrous ferric oxide, etc.
2. Industrial wastes like fly ash, bio gas slurry, chrome sludge, furnace slag etc.

3. Agricultural wastes like coconut shell, banana pith, orange peel, soya cake, olive cake, hazelnut shell, rice husk, sawdust and in many cases their carbonized products.
4. Forest wastes like barks, leaves and in many cases their carbonized products.
5. Aquatic plants like weeds, algae, etc.

These low-cost materials can be used as adsorbents with little processing. This would improve economic value, helping industries to reduce the cost of waste disposal and provides a potential alternative to activated carbon.

1.9 Review of Literature-Removal of Heavy Metals using various adsorbents

1.9.1 Natural Materials

Natural materials such as zeolite and clay minerals which are locally available and low-cost adsorbents have been explored for treating metal contaminated wastewater due to their metal binding capacity. Erdem, Karapinar and Donat⁹² studied Co (II), Cu (II), Zn (II) uptake from metal finishing wastewater using natural zeolite. Wingenfelder et al.,⁹³ suggested that the Cr(VI) adsorption capacities of zeolite varied, depending on the extent of chemical treatment. Lagergren and second order kinetic models were successfully described for the adsorption behaviour of Ni(II) onto zeolite⁹⁴. The hydroxyapatite/ Zeolite composites were synthesized by precipitation method and used as an adsorbent for the removal of Co(II) ions from aqueous solutions⁹⁵.

Stella Tryanatafillou et al.,⁹⁶ experimented the removal of Ni(II) and Co(II) removal from aqueous solution by Na activated bentonite. Adsorption of Ni(II), Cd(II), Cr(III) and Mn(II) from synthetic aqueous solution by Brazilian natural scolecite⁹⁷ was best described by Freundlich isotherm model. Jordan low-cost zeolite and bentonite⁹⁸ was used for the removal of Co(II) and Ni(II). Reyad A. Shawabkeh et al.,⁹⁹ reported that adsorption isotherms for both Co(II) and Zn(II) onto chemically treated bentonite fitted well with Langmuir, Freundlich and Redlich-Peterson models. The percent removal of cesium, cobalt, lead and

copper onto activated bentonites were seriated in the order Na- bentonite > K- bentonite > T- bentonite > n- bentonite by Abdel Geleel.¹⁰⁰

Omer Yavuz et al.,¹⁰¹ studied the sorption of Co(II), Ni(II), Mn(II) and Cu(II) onto kaolinite, where the systems exhibited linear fit of Langmuir adsorption equation. Kaolinite and Montmorillonite had been used as adsorbents for Fe(III), Co(II) and Ni(II) in aqueous medium by Krishna G.Bhattacharya et al.,¹⁰² Adsorptive removal of Cu(II) and Ni(II) from Jebel Chakir land fill leachate onto smectite rich clayey rock were carried out using both column and batch methods by Islem chari et al.,¹⁰³

S.Rengaraj and Seung- Hyeon Moon¹⁰⁴ carried out studies on the removal of Co(II), Ni(II) and Cr(III) from aqueous solutions using IR N77 resin. Reversible first order kinetics favored the sorption of Ni(II) onto ceralite IR 120 cation exchange resins as reported by Senthilkumar et al.,¹⁰⁵. Adsorption kinetics of Ni(II) on modified Duolite XAD-761 resin was best described by pseudo second order model as reported by Tharanitharan et al.,¹⁰⁶

Palygorskite clay, mined in the Dwaalboom area of the Northern Province of South Africa, was used as an adsorbent for the removal of heavy metal ions such as Pb(II), Ni(II), Cr(VI) and Cu(II) from aqueous solutions¹⁰⁷. The Cr(VI) removal from simulated wastewater using pyrites was investigated by Zouboulis et al.,¹⁰⁸. Ni(II) and Cu(II) removal from synthetic solutions and real wastewater using natural vermiculite was also examined¹⁰⁹.

The ability of Clinoptilolite powder to adsorb Ni(II) ions from wastewater was investigated through batch experiments by M.H.S. Ismail et al.,¹¹⁰ Langmuir's and Freundlich's isotherm models adequately described the adsorption process for the removal of Cr(VI), Cu(II), Ni(II) and Zn(II) from water by Slovakite adsorbent¹¹¹.

1.9.2 Industrial By-products

Inexpensive and abundantly available industrial by-products such as waste iron¹¹² and hydrous titanium oxide¹¹³ were used to remove Cr(VI) metal from wastewater by different

researchers. Use of lignin from Kraft black liquor obtained from pulp paper industry and activated lignin have been employed by Rajalakshmi et al¹¹⁴ for the removal of Ni(II) from wastewater.

Zouboulis and Kydros¹¹⁵ investigated red mud, a solid by-product from alumina production, for Ni(II) removal from simulated water. Fly ash was evaluated for Ni(II) and Cu(II) removal from wastewater¹¹⁶. South-African coal fly ash had been reported as a potential alternative to remove Co(II) from synthetic wastewater.¹¹⁷

The performance of hydrogen peroxide treated bagasse fly for the removal of Pb(II) and Cr(VI) was investigated by Gupta and Imran Ali¹¹⁸. Vimal Chandra Srivastava et al., studied the competitive adsorption of Cd(II) and Ni(II) onto bagasse flyash¹¹⁹. Sewage sludge ash was utilized as a potential sorbent for the removal of Ni(II) and Cd(II) from aqueous solutions as reported by Zouhair Elouear et al.,¹²⁰

1.9.3 Agricultural Wastes

India is an agrarian country and preconsumer processing agricultural waste is available in abundance. Agricultural wastes can be effectively used as adsorbents for the removal of heavy metals from wastewater. There are currently a large number of studies regarding the use of several agricultural wastes to sequester heavy metal ions. To enhance the chelating efficiency of metal ion, these wastes are pretreated, using different agents, like base solutions, minerals and organic solutions, organic compounds and oxidizing agents¹⁸³.

Rice husk, an abundantly available agricultural waste, was used to trap heavy metals in either untreated or modified form. Uptake of Ni(II) from aqueous solutions by rice husk¹²¹ has proved it to be a potential adsorbent. The adsorption of Ni(II) and Cd(II) ions onto rice straw¹²² was investigated by G.O.El Syed et al., Husk of Toor dal (*Cajanus cajan*) was employed by N.Ahalya et al.,¹²³ to remove Cr(VI) and Fe(III) ions from aqueous solutions.

Sawdust, a waste product obtained from wood industry can be used as a low-cost adsorbent for the removal of heavy metals, largely due to its lignocellulosic composition.

Beech saw dust *Fagus orientalis* L, was elaborately examined for the removal of Cr(VI) by F.N.Acar and E.Malkoc,¹²⁴. The ability of maple saw dust was studied by Shyam S.Shukla et al.,¹²⁵ for the removal of Ni (II) ions from aqueous solutions.

Wheat bran, a by-product of wheat milling industries was elaborately examined for its sorption capacity on Cr(VI) from aqueous solutions by M.Nameni et al.,¹²⁶ Maize bran and wheat residue carbon were utilized for the sorption of Cr(VI) wherein the adsorption was effective at lower pH range and at higher temperatures^{127,128}.

The removal of Ni(II) using peanut hulls has been reported³³. Removal of Ni(II) and Cr(VI) from aqueous solutions by hazelnut shell activated carbon were studied by Kobya et al.,^{129,130}. The adsorption ability of hazelnut, almond and walnut shells were examined for the control of Ni(II), Cd(II), Pb(II), Cr(VI) and Hg(II) ions from aqueous and industrial liquid streams in different studies^{131,132,133}. Almond green hull, an agriculture solid waste, was found to be rapid in the removal of Co(II) from aqueous solutions by A. Ahmad Pour et al.,¹³⁴ The ability of *C. albidum* seed to adsorb metal ions like Ni(II), Cu(II), Zn(II) and Pb(II) was investigated by Oboh et al.,¹³⁵ Adsorption capacity of almond, apricot shells and activated carbon onto Cr(VI) was investigated in a batch system by Khazaei et al.,¹³⁶

Some more low cost adsorbents reported for Cr(VI) removal were zinc chloride activated *Terminalia arjuna* nuts¹³⁷, phosphoric acid activated tamarind hulls¹³⁸, sulphuric acid activated ground nut husk¹³⁹, date palm seeds¹⁴⁰, tamarind seeds¹⁴¹ and chitosan coated sapotaceae seed shells¹⁴². Removal of Ni(II) from aqueous solutions have been studied by P.E.Aikpokpodion et.al¹⁴³ and Umesh K.Garg et.al employing tea waste powder and sugarcane bagasse respectively¹⁴⁴. Both Langmuir and Freundlich adsorption models confirmed the adsorption equilibrium of Cr(VI) onto cooked tea dust as reported by Dhanakumar et al.,¹⁴⁵

Jamil Anwar et al., carried out the batch mode sorption study of Cr(III) employing *Polyalthia longifolia* leaves biomass¹⁴⁶. Piyush Kant Pandey et al., investigated the

biosorptive removal of Ni(II) from wastewater and industrial effluents employing fresh and chemically treated biomass of *Calotropis procera*¹⁴⁷. Batch adsorption experiments were performed to study adsorption potential of agricultural residues viz. rice straw, wheat straw and *Salvinia* plant biomass¹⁴⁸ for removal of heavy metals such as Cr(VI), Ni(II) and Cd(II). Mohammed Iqbal and Saeed Iqbal Zafar reported the adsorption studies of Ni(II), Pb(II) and Zn(II) from aqueous solution on dried biomass of petiolar-felt sheath of palm¹⁴⁹. The kinetics of biosorption of Pb(II) and Cr(VI) ions onto *Ficus religiosa* leaves biomass was well described by the pseudo second order model¹⁵⁰.

Low cost agricultural by-products like coconut husk and teak tree bark were used as adsorbents in the removal of Cr(VI) and Ni(II) from aqueous solutions by O.O.Kehinde et al.,¹⁵¹ The removal of Cr(VI) and Cr(III) from aqueous solutions utilizing sugarcane pulp residue was reported by Zhi-Hui Yang et al.,¹⁵²

B.V.Babu et al.,¹⁵³ studied the kinetics of adsorption of Cr(VI) using activated neem leaves. The ability of neem leaves to adsorb metal ions like Cu(II), Pb(II), Ni(II) and Zn(II) was tested by Innocent Oboh et al.,¹⁵⁴ *Azadirachta indica* (neem) leaf powder was used as an adsorbent for the removal of Cr(VI) from aqueous solution by Venkateswarlu et al.,¹⁵⁵ Langmuir equation is found to best represent the equilibrium data for Cr(VI)- pine needles powder system as reported by Mohammad Reza Hadjmohammadi et al.,¹⁵⁶ Rudre Gowda utilized coconut leaves as an alternate adsorbent for the removal of Ni(II) from electroplating effluents¹⁵⁷. P.Senthil Kumar & K.Kirthika employed bael tree leaf powder for the removal of Ni(II) from aqueous solution¹⁵⁸. The batch-wise biosorption of Co(II) by peepal leaf powder was well supported by Freundlich, Langmuir, Redlich-Peterson and Tempkin isotherm models indicating favourable biosorption as reported by Krishna & Venkateswaralu¹⁵⁹. The surface sorption abilities of powdered leaves and ashes of *Achyranthes aspera*, *Mentha*, *Embilica officinalis*, *Azadirachta indica*, *Hibiscus rosa sinensis*

and *Ocimum sanctum* was explored for the removal of heavy metal ions by Krishnaveni and Ravindranath¹⁶⁰

N.M.Rane et al., experimented the use of naturally available low cost adsorbents for the removal of Cr(VI) from waste water¹⁶¹. Sahare A.B reported the removal of Cu(II) and Ni(II) from aqueous solution using mango tree bark¹⁶². A.Manjusha et al.,¹⁶³ studied the sorption capacity of *Mangifera indica* bark dust to trap Cr(VI) from aqueous solutions. The potential to remove Ni(II) from aqueous solutions through adsorption using gulmohar tree bark was investigated by A.K.Patil et al.,¹⁶⁴ Rice straw, rice bran, rice husk, hyacinth roots, neem bark, saw dust of teakwood origin, neem leaves and co-conut shells were used as low cost natural or agricultural wastes for Cr(VI) removal from aqueous solutions¹⁶⁵

1.9.4 Agriculture-Industrial Wastes

Tea factory waste was assessed for its sorption capacity in the removal of Ni(II)¹⁶⁶ and Cr(VI)¹⁶⁷ by Emine Malkoc et al., Chemical activation of coir pith by ZnCl₂ was carried out for the removal of Cr(VI), Ni(II) and Hg(II) from wastewaters¹⁶⁸. Another coir based adsorbent puresorbe was studied by Nityanandi et al.,¹⁶⁹ to trap Cr(VI) ions. Coconut husk was examined by Syed Moosa et al.,¹⁷⁰ in the uptake of Cd(II), Cr(III) and Hg(II) from aqueous solutions.

Adsorption of Cr(VI) onto sawdust of aspen tree and activated sawdust was investigated in a batch system by H.T.Hamed Mosavian et al.,¹⁷¹ Freundlich isotherm fitted the experimental data better than the Langmuir isotherm in the characterization of the adsorption of Ni(II) ions onto pine sawdust as reported by Krishnie Moodley et al.,¹⁷² M. Malakootian et al.,¹⁷³ reported the efficiency of wood ash to remove Pb(II) and Co(II) from paint effluents. The potential of *Pinus roxburghii* bark collected from the joinery mills as an adsorbent for heavy metals such as Cr(VI), Ni(II), Cu(II), Cd(II) and Zn(II) from aqueous solution was investigated by Rais ahmed et al.,¹⁷⁴

1.9.5 Aquatic plant Wastes

The study on effectiveness of *Eichhornia crassipes* was carried out to adsorb metal ions such as Fe^{3+} , Cu^{2+} , Zn^{2+} , Cr^{3+} , Cd^{2+} ¹⁷⁶ and Pb^{2+} ¹⁷⁵. The metal binding potential of seven different aquatic weeds has been reported for the adsorption of Cr(III) and Cr(VI)¹⁷⁷. Acid treated brown seaweed *Ecklonia sp* was examined as a potential sorbent for Cr(VI) removal by Donghee Park et al.,¹⁷⁸

The mechanism of simultaneous metal removal by three macrophytes biomass *Spirodela intermedia*, *Lemna minor*, *Pistia stratiotes* was investigated by Patricia miretzky et al.,¹⁷⁹ The dried biomass of *Oscillatoria laete-virens* was found to possess the sorption ability to trap heavy metals like Cr(VI) and Ni(II) in polluted water¹⁸⁰. Batch adsorption studies for the removal of Ni(II) from aqueous solutions utilizing the biomass of *Azolla filiculoides* were experimented by Salman Ahmady Asbchin et al.,¹⁸¹. Smita Samdani et al.,¹⁸² reported that ligand exchange mechanism was responsible for the high Cr(VI) adsorption capacity of *Hydrilla verticulata*.

1.9.6 Modified Agricultural Wastes

The efficiencies of boiled and formaldehyde treated rice husk¹⁸³ was investigated for adsorption of Cr(VI). Hui Gao et al., observed that carboxyl groups present on the biomass of rice straw played an important role in Cr(VI) remediation¹⁸⁴.

Garg et al.,¹⁸⁵ employed formaldehyde and sulphuric acid treated sawdust of Indian rosewood, (*Dalbergia sissoo*) for the removal of Cr(VI). They compared the adsorption efficiencies of sawdust with commercially available coconut shell based activated carbon and proposed that the treated sawdust was a more potential adsorbent than commercial activated carbon. Raw banana peels and phosphoric acid activated bael fruit shells were used to remove Cr(VI) from aqueous solutions and industrial wastewater^{186, 187}.

Mehmet Emin Argun et al., found that Langmuir and D-R isotherms could be used to model isothermal sorption of Cu(II), Ni(II) and Cr(VI) on acid modified oak sawdust¹⁸⁸.

The removal of Cr(VI) from aqueous solution was studied by Babel et al.,¹⁸⁹. Amudha et al.,¹⁹⁰ developed composite adsorbents such as chitosan coated and acid treated coconut shell carbon and studied their effectiveness in the removal of zinc from aqueous solution.

Coconut coir pith modified with cationic surfactant was tested for the removal of Cr(VI) from electro plating effluents¹⁹¹. The potential of a lignocellulosic fibre, jute, was assessed for adsorption of heavy metal ions like Cu(II), Ni(II) and Zn(II) from their aqueous solutions by S.R. Shukla et al.,¹⁹² The kinetics and intraparticulate diffusivities for the adsorption of Co(II), Fe(II), Cu(II) onto modified and unmodified maize cob was investigated. The trend of the sorption capacity was found to be Co(II) > Fe(II) > Cu(II) for unmodified and Co(II) > Cu(II) > Fe (II) for EDTA modified maize cob¹⁹³. Cu(II) adsorption by orange peel was investigated by Feng Ning-chuan et al.,¹⁹⁴ involving sodium hydroxide modification. S.J Patil et al.,¹⁹⁵ employed modified powdered Indian babul bark to adsorb Ni(II) ions.

1.9.7 Nano hydroxyapatites

More recently, hydroxyapatite has been proposed as an inexpensive but efficient adsorbent for removal of heavy metal ions from aqueous solution¹⁹⁶. The high sorption capacity for heavy metals, low water solubility and high stability under reducing and oxidizing conditions, availability and low cost are the principal characteristics of the hydroxyapatite in its utilization as material for ions retention from solutions. It was conducted in stabilization of a wide variety of metals viz., Cr, Co, Cu, Cd, Zn, Ni, Pu, Pb, As, Sb, U and V by many investigators¹⁹⁷. They reported that the sorption had taken place through ion-exchange reaction, surface complexation with phosphate, calcium and hydroxyl groups and/or co-precipitation of new partially soluble phases.

Wang and Chen¹⁹⁸ reported the greater capability of Fe₂O₃/HA to adsorb Cd(aq), Pb(aq), Cu(aq) which has indicated its potential use as another promising way to remediate metals-contaminated water. The results indicated that the sorption of Cd, Pb and Cu ions by the nano-particles can be fitted well using Langmuir isotherm.

The ability of nano-hydroxyapatite (nano-HAP) to adsorb aqueous Cd, Pb and Cu ions from single-metal and multi-metal ions reaction systems were reported by S.B.Chen et al¹⁹⁶. The measured selectivity coefficient in multi-metal (Cd–Pb–Cu) reaction systems shows that Pb has the highest sorption selectivity on nano-HAP among the metals investigated. calcium hydroxyapatite (CaHAp), Ca₁₀(PO₄)₆(OH)₂, is used for the removal of heavy metals from contaminated soils, wastewater and fly ashes¹⁹⁷. Maria Ignat et al., investigated the removal of Zn²⁺ ions using hydroxyl apatite nanoparticles¹⁹⁹. The correlation coefficient value of the Zn²⁺ ions adsorption on this Calcium HAp nanomaterial represented a good fitting of experimental data. The sorption of lead solution by synthetic hydroxyapatite was experimented by S.Bailliez et al²⁰⁰. It was shown that the dissolution of hydroxyapatite is followed by the formation of hydroxypyromorphite, a solid solution of Pb_{10-x}Ca_x(PO₄)₆(OH)₂ formula, with Pb ions mostly occupying Ca(II) sites, and that the Ca/P molar ratio of this solid solution decreases continuously.