REVIEW OF LITERATURE

2. REVIEW OF LITERATURE

The review of literature pertaining to the present investigation is organized and presented under the following headings:

2.1. Physicochemical and biological properties of nickel

2.2. Nickel pollution and its toxicity

2.3. Bioremediation of heavy metals

2.4. Process of microbial metal uptake and detoxification of toxic materials

2.5. Impact of water pollution on plant growth

2.6. Effect of industrial effluents on soil parameters

2.7. Effect of pollutants on the biochemical constituents and histology of fishes

2.1. PHYSICOCHEMICAL AND BIOLOGICAL PROPERTIES OF NICKEL

2.1.1. Physical and biological properties of nickel

Nickel is one of the essential elements found in abundance in the earth's crust occurring at an average concentration of about 75µg/g. It is a metallic element belonging to group VIII b of the periodic table. It is hard, silvery-white, lustrous and found in nature as a component of silicate, sulfide or arsenide ores. It's atomic number is 28, atomic weight is 58.71, specific gravity is 8.9 with the melting and boiling points of about 1.455°C and 2.732°C respectively. It has high electrical and thermal conductivity and is resistant to corrosion at ambient environmental temperatures between -20°C and +30°C and is therefore often electroplated as a protective coating (Chau and Cordeiro, 1995). Although it has oxidation state of -1, 0, +1, +2, +3

and +4, it exists principally in the divalent state (Ni^{2+}) and it is the stable form in the environment. In biological systems, nickel in its ionic state forms stable complex components with various ligands and bind to organic material (Fordsmand, 1997).

2.1.2. Biological properties of nickel

Nickel is considered to be an essential element in animals, microorganisms, plants and has been a constituent of enzymes and proteins. In acetogenic bacteria the reduction of carbon monoxide to acetate is dependent on nickel which is needed for activation and synthesis of carbon monoxide dehydrogenase (Drake, 1982). Nickel stimulates the growth of *Acetobacterium woodii* on the medium supplemented with fructose. Nickel is the core metal in the tetrapyrrole ring of methanogenic bacteria which is essential for the growth of these microbes. Nickel is essential for the active synthesis of urease in plant cells. In several species of higher plants such as jack beans (*Canavalia* sp.), soybeans (*Glycine max*), rice (*Oryza sativa*), and tobacco (*Nicotiana tabacum*), it is required for effective urea metabolism and urease synthesis (Kasprzak, 1987). Some terrestrial plants, such as *Alyssum* species accumulate nickel and require it for growth (Baker *et al.*, 2000). Welch (1995) reported that nickel is required in low concentrations by legumes dependent on symbiotically fixed nitrogen either for the growth of rhizobia or for the utilization of fixed nitrogen or both.

Nickel is required for iron absorption, seed germination and its deficiency leads to the production of viable seeds in plants. Application of nickel to crops protects them from certain yield limiting diseases, thus potentially reducing pesticide usage and improving crop yield. Nickel also acts as a bio control agent for microbial pests. It is a key factor affecting the production of secondary plant

metabolites and thus influencing plant resistance to disease (Wood and Reilly, 2007). High concentrations of nickel inhibited the formation of IAA, tryptophan and simultaneously promoted the formulation of phenolic and terpenoid inhibitors (Tikhomirov *et al.,* 1987). Khan and Moheman (2006) reported that nickel interacts with iron found in the hemoglobin and helps in oxygen transport, stimulates the metabolism and regarded as a key metal in several plants and animal enzyme systems. Nickel is involved in the transmission of genetic code (DNA, RNA) and it is also present in certain enzyme systems that metabolize sugars.

Nickel can substitute for calcium in excitation process and in the binding with membrane ligands such as the phosphate groups of phospholipids in the process of nerve transmission, muscle excitation and contraction (Howard, 2003).

Nickel exists in human and rabbit serum as three forms namely, nickel bound to ultrafilterable ligands, albumin bound nickel and macroglobulin bound nickel. Albumin is the main transport protein for nickel in human, rat and bovine sera. A metalloprotein termed nickeloplasmin has been isolated from the sera of rabbits (α-2 macroglobulin) and human (α-glycoprotein) (USPHS, 1993).

Ultrafilterable nickel binding ligands play an important role in extracellular transport and in the elimination of nickel in urine. L - histidine was identified as a low molecular mass nickel binding constituent of human serum which has greater affinity for nickel than serum albumin. It has been found that L - histidine nickel complex has smaller molecular size than the albumin nickel complex which mediates the transport through a biological membrane by virtue of the equilibrium between these two molecular species of nickel. The exchange and transfer of nickel between L - histidine and albumin

appears to be mediated by a ternary complex in the form of albumin nickel L - histidine (Sigel and Sigel, 1988).

Nickel is an essential nutrient in 17 animal species, including chicken, cow, goat, pig, rat and sheep (IPCS, 1991). At very low levels, nickel is also an essential element to humans (Wintz *et al.*, 2002). Schnegg and Kirchgessner (1980) reported that nickel deficiency in rats led to reduced iron content in organs, reduced haemoglobin and hematocrit values and anaemia. King *et al.* (1985) suggested that nickel might serve as a cofactor for the activation of calcineurin, a calmodulin dependent phosphoprotein phosphatase.

Nickel has an essential function in the action or formation of cGMP, a signaling agent that regulates various physiological processes such as blood pressure control, sperm physiology, sodium metabolism and cardiovascular health. Nickel is consistently present in RNA and is bound to several biological substances such as proteins (keratin, insulin), amino acids and serum albumins. It also activates enzymes like arginase, trypsin, acetyl coenzyme A, carboxylase and synthetase (Yokoi *et al.*, 2002).

2.2. NICKEL POLLUTION AND ITS TOXICITY

2.2.1. Sources and occurrence of nickel

Nickel is a naturally occurring element that is present in soil, water, air and biological materials. It is a natural component of earth's crust and is present in igneous rocks (Chauhan *et al.*, 2008). Natural sources of nickel include dusts from volcanic emissions and the weathering of rocks and soils (Kasprzak *et al.*, 2003). Inorganic fertilizers particularly phosphate fertilizers have variable levels of nickel depending on their resources (Sharma and Agarwal, 2005).

Atmospheric nickel is considered to exist mainly in the form of aerosols with different concentrations of nickel particles depending on the type of sources. A part of atmospheric nickel entering into the environment originates from meteoric dusts, smoke particles from forest fires, volcanic ash, windblown soil dusts and aerosols from oceanic dusts (Ross, 1994).

Although nickel occurs naturally, concentrations found in the environment may also be caused by anthropogenic input such as depositions from the burning of fossil fuels (IARC, 1990), energy supplying power stations (coal burning power plants, petroleum combustion, nuclear power stations and high tension lines) (Verkleji, 1993), chemical industries (pigment manufacturing, plating/metal finishing, cement manufacturing) and metallurgical industries (steel manufacturing, ore refining and alloy manufacturing). The lubricants which are antiwear protectants for vehicles emit nickel from inefficient engines during the transportation (Sharma and Agarwal, 2005). Nickel is also used as a catalyst in oil refining process, in cryogenic containers, in pollution abatement equipments and also as a component of some plumbing materials. When pipes and other materials corrode, nickel can be released to drinking water and may cause damage to human health, but the releases from this source are small. Oats, chocolate, soy beans, nuts and other whole grains are excellent sources of nickel (Salniko *et al.*, 2003).

Nickel occurs in aquatic system as soluble salts adsorbed on clay particles or organic matter (detritus, algae, bacteria) or associated with organic particles such as humic acid, fulvic acid and proteins. Nickel may enter surface water as a particulate matter in rain water, through the dissolution of primary bedrock minerals and from anthropogenic sources or from secondary soil phases (Boyel, 1981).

2.2.2. Nickel toxicity and health hazards

Although nickel is omnipresent and is vital for the function of many organisms, concentrations in some areas from both anthropogenic release and naturally varying levels may be toxic to living organisms.

Waste water discharged from electroplating, electronics and metal cleaning industries often contains high concentration of nickel ions and causes various types of acute and chronic disorders (Akhtar *et al.*, 2004).

In humans, nickel is known to cause liver, kidney, spleen, brain and tissue damage, vesicular eczema, lung and nasal cancer on acute exposure (IPCS, 1992). Nickel induces embryotoxic and nephrotoxic effects, allergic reactions and contact dermatitis (EPA, 2002). Nickel sensitization also occurs in general population from exposure to coins, jewellery, watchcases, and clothing. It causes conjunctivitis, eosinophilic pneumonites, asthma and local or system reactions to nickel containing prostheses such as joint replacement, cardiac valve replacements, cardiac pacemaker wires and dental inlays (Hostynek and Maibach, 2002).

Nickel compounds are carcinogenic to humans and they accumulate in the nucleus, especially in the nucleolar fraction (NAS, 1975). Intracellular binding of nickel to nuclear proteins, RNA and DNA may cause strand breakage, induce chromosomal aberrations, sister chromatid exchange, diminished RNA synthesis, mitotic activity and gene expression in both mammalian and human cultured cells (Zienolddiny *et al.*, 2000). Matlock *et al.* (2002) observed the transformation of tumorous cells which involves DNA

damage resulting from mutation caused by hydroxy radical or other oxidizing species.

Acute exposure of human lungs to nickel results in pathological pulmonary lesions, hemorrhage, edema, deranged alveolar cells, degeneration of bronchial epithelium and pulmonary fibrosis. When the skin surface is exposed to nickel ions, it diffuses through the epidermis and binds to the carrier proteins to form allergen which causes skin disorders and allergies (Grimsrud *et al.*, 2003). Nickel penetration into the skin is also found to be enhanced by sweat, blood, detergents and other body fluids (USEPA, 1980). Nickel compounds have been found to penetrate the mammalian placental barrier and affect the foetus in relevance to the presence of female workers in industry (Sunderman *et al.*, 2001).

Nickel is a potent animal teratogen. Inhalation and exposure of nickel carbonyl compounds to rats and hamsters were found to cause fetal death, decreased weight gain and eye malformations (Sevin, 1980). Nickel was also proved to be embryolethal and teratogenic to white leghorn strains of the domestic chicken (*Gallus* sp.), possibly due to the mitosis - inhibiting activity of nickel compounds. Malformations might include poorly developed or missing brain and eyes, everted viscera, short and twisted neck and limbs, hemorrhaging and reduction in body size (Gilani and Marano, 1980). Rodents exposed to nickel during gestation showed a decline in the frequency of implantation of fertilized eggs, enhanced resorption of fertilized eggs and foetus, an increased frequency of stillbirths and growth abnormalities in live-born young (Hausinger, 1993).

Release of nickel effluents into the water bodies was reported to cause stress to aquatic animals and affect their metabolic and

physiological activities, biochemical composition and histology of tissues (More *et al.*, 2003). Nickel toxicity in plants cause patchy discolourations, premature senescence, yellowing of old leaves, stunting of the roots, deformation of various plant organs, necrosis of leaves, wilting, growth reduction, wrinkled and cupped leaves, shortened internodes resulting in stunted plants and witches broom appearance referred to as "mouse ear" disorder (Fordsmand, 1997). It was also found to affect the photosynthesis, cell divisions and act as a mutagen to plants.Some species of plants accumulate higher doses of nickel above ground tissues. These hyperaccumulators tolerate high levels of nickel due to free histidine in the xylem sap, which also provides a defense mechanism against herbivory (Kramer *et al.*, 1996).

In microorganisms, nickel was seen to bind mainly to the phosphate, carboxylic and hydroxycarboxylic groups of the cell walls. From this site, an active transport mechanism designed for magnesium was observed to transport nickel. In microorganisms and higher plants, magnesium is considered as the usual competitor for nickel in the biological ion-exchange reactions (Kasprzak, 1987).

2.3. BIOREMEDIATION OF HEAVY METALS

In recent years, developing countries are increasingly concerned with pollution due to the presence of toxic heavy metals in the environment. The need for clean environment has stimulated interest in finding alternative methods for decontamination of toxic residues, pollution removal and waste disposal. Nowadays various physicochemical methods are available for the removal of heavy metal ions from industrial waste water which include chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange and

membrane technologies, but these techniques are likely to become increasingly expensive and inefficient (Devarajan and Sulaiman, 2005). To overcome these problems, biological methods such as biosorption, bioaccumulation, biodegradation and bioremediation are used for the removal of heavy metal ions which provide an attractive alternative to the physicochemical methods (Wang and Chen, 2009) and these methods are potentially simple, low cost, more effective, ecofriendly and a self sustaining option for amelioration of waste water which is receiving new attention nowadays (Jothimani and Bhaskaran, 2003).

Bioremediation is a pollution control technology that uses microorganisms or plants to catalyze the degradation or transformation of various toxic chemical compounds to less toxic forms (Murugesan and Vasanthy, 2003).

2.3.1. Criteria for bioremediation

To consider bioremediation as a practical means of treatment certain criteria must be met

- The organisms must have the necessary catabolic activity to degrade the contaminant at a reasonable rate to bring its concentration to a level that meets regulatory standards.
- The target contaminant must be bioavailable.
- The contaminated site must have conditions conducive for microbial or plant growth or enzymic activity.
- The cost of the bioremediation must be less or not more expensive than other technologies that can also remove the contaminants (Ramasamy and Thanga, 1999).

2.3.2. Bioremediation techniques

The goal of microbial remediation of heavy metal contaminated soils and sediments are to immobilize the metals to reduce its bioavailability and mobility to remove them from the soil (Rajendran *et al.*, 2003).

Bioremediation technologies are classified into *in situ* or *ex situ* bioremediation. *Ex situ* bioremediation involves the removal of contaminated material to another area for treatment. Bioreactors, land farming, composting, biopiles and some forms of solid - phase treatment are examples of *ex situ* bioremediation techniques. *In situ* bioremediation involves treating the contaminated material at the place of discharge or site and the examples include biosparging, bioventing, bioaugmentation and biostimulation (Lloyd and Lovely, 2001).

The use of polyphasic approach involving a combination of molecular biology techniques, microbiological methods and geochemical techniques or microsensors are now being employed to study bioremediation, since a comprehensive understanding of microbial ecology is required to gain maximum benefits from this process (Ramsing *et al.*, 1996).

2.3.3. Selection of microbes for bioremediation

Microbes have emerged as the most effective scavengers of heavy metals (Ali *et al.*, 2009). Nowadays, new technologies are constantly being sought for removing heavy metals and toxic substances from waste water so that they can be safely discharged (Kumar *et al.*, 2008). Microorganisms related treatment technologies may provide an alternative or adjunct to conventional techniques for metal removal or recovery.

Microbial interactions with heavy metals offer numerous opportunities of exploiting the 'tiny animalcules' for environmental clean-up. Different types of microorganisms such as bacteria, cyanobacteria, algae, fungi and yeasts remove the heavy metals from the solutions having an array of defense mechanisms, which keep metal ions trapped outside or inside the cells (Paknikar *et al.*, 2003).

For successful bioremediation, the biosorbent or the microorganism should posses the following ideal properties:

- ❖ It should sequester toxic metal ions both from dilute and concentrated solutions.
- ❖ It should not face antagonism with essential metal ions.
- ❖ It should be reusable.
- ❖ It should not by itself contaminate the environment (Akthar *et al.*, 1996).

2.3.4. Mechanism of microbial metal tolerance

Microorganisms respond to heavy metal stress using different defense mechanisms such as exclusion, compartmentalization, formation of complexes and synthesis of binding proteins like metallothioneins and phytochelatins. Ochari (1997) has divided the general toxicity mechanism for metal ions into three categories:

- Blocking the essential functional groups of biomolecules especially proteins and enzymes.
- Displacing the essential metal ions in biomolecules.
- Modifying the active conformation of biomolecules resulting in the loss of specific activity.

Microorganisms can affect heavy metal concentrations in the environment because they exhibit a strong ability for metal removal from solution and this can be achieved through either enzymic or nonenzymic mechanisms (Nealson *et al.*, 1992). Avoidance, restriction of metal entry into the cell, either by reduced uptake or active efflux or by the formation of complexes outside the cell and sequestration, reduction of free ions in the cytosol either by the synthesis of ligands to achieve intracellular chelation or by compartmentalization are the strategies of microorganisms to protect themselves against heavy metal toxicity (Tomsett *et al.*, 1992).

2.3.5. Metal removal by living and dead biomass

Recently environmental pollution with anthropogenic sources of metals has increased the need for research concerning the microbial metal removal as well as remediation. Many researchers have studied the uses of living and non living (dead) microorganisms for metal reclamation and remediation of contaminated soils and water (Lakshmi *et al.*, 2007).

Two types of metal binding to biomass based materials can take place; these are passive binding in both living and nonliving cells by very rapid physical adsorption and ion exchange with the cell surface, and active binding in living cells by slower metal uptake as a result of metabolic activity (Dursan, 2006).

Both live and dead cells of microorganisms are capable of metal accumulation, but there are differences in the mechanisms involved, based on the extent of metabolic dependence (Malik, 2004). Systems using living cells are likely to be more sensitive to metal ion concentration operating conditions like pH, temperature, the recovery and regeneration of the biosorbent is more complicated

(Kumar *et al.*, 2008) whereas the dead biomass accumulates heavy metals to nearly same or greater extent than the living cell (Vijayaraghavan and Yun, 2008). The use of dead biomass is advantageous over living cells because of the ease in its handling, its ability to withstand toxicity, adverse operating conditions, costly nutrients are not needed, no physiological constraints like live biomass, process is very rapid, aseptic maintenance is not required, recovery is faster and more concentrated (Kumari and Abraham, 2007).

2.4. PROCESS OF MICROBIAL METAL UPTAKE AND DETOXIFICATION OF TOXIC MATERIALS

Once the metals enter the environment, they may undergo transformation into various mobile forms or get immobilized. Biological activity accounts for a large number of the environmental sinks of toxic metals, whether these are derived from natural or anthropogenic sources. Metal deposition by microorganisms is of great importance in biogeochemical cycles. In recent years, biosorption, a process which utilizes inexpensive dead or live microbial biomass to sequester metals from industrial effluents has gained importance due to its good performance, low cost, specificity, minimum sludge generation and amenability for repeated use (Prigione *et al.*, 2008). Biosorption is the ability of biological materials to accumulate heavy metals from waste water through metabolically mediated or physicochemical pathways of uptake (Volesky and Naja, 2005).

2.4.1. Biosorption based on the dependence of cell metabolism

The complex structure of microorganisms implies that metal uptake may be either metabolism independent or dependent process.

2.4.1.1. Metabolism independent biosorption

During metabolism independent process, metal uptake is by physicochemical interactions between the metal and functional groups present on the microbial cell surface. This mechanism of biosorption is complex mainly involving ion exchange, chelation, complexation, adsorptions by physical forces, ion entrapment in inter and intra fibrillar capillaries and spaces of the structural polysaccharide network as a result of diffusion through cell walls and membranes. Several active groups of cell constituents like acetamido group of chitin, structural polysaccharides of fungi, amine (amino and peptidoglycosides), sulphydrl and carboxyl groups in proteins, phosphodiester (teichoic acid), phosphate, hydroxyl groups in polysaccharides participate in biosorption. This type of biosorption is relatively rapid and can be reversible (Vasudevan *et al.*, 2001). The metal ions bind to the cell surface either by electrostatic interactions, vanderwaals force, covalent bonding, redox interactions, extracellular precipitation, nucleation or combination of these processes (Blanco, 2000). The predominant mechanism reported for the accumulation of heavy metals in bacteria, fungi and algae are:

Biosorption by bacteria

There is a great deal of heterogeneity among different bacterial species in relation to the number of surface binding sites, binding strength for different ions and binding mechanisms. Gram positive bacterial cell walls and surfaces have a negative charge density owing to the peptidoglycan network, a network consisting of strands of alternating glucosamine and muramic acid residues which are N-acetylated. Carboxylate groups at the carboxyl terminus of individual strands provide bulk of anionic character to the cell wall. The anionic nature of bacterial surface enables them to bind

metal cations through electrostatic interactions (Srivastava and Thakur, 2003).The phosphodiesters of teichoic acid and the carboxyl groups of teichuronic acid contribute to the ion-exchange capacity of cell wall. In comparison to ion exchange process, bacteria possess higher metal binding capacities attributed to nucleation reaction (Prescott *et al.,* 2002). Due to all these properties Gram positive bacteria have high capacity of metal binding. The cell envelope of Gram negative bacteria is structurally more complex than the Gram positive bacteria. The cell wall structure consists of two membranes separated by periplasm. The major anionic character in Gram negative cell walls is due to the phosphate group in outer and inner membranes, thin peptidoglycan layer and the metal ions bind to phosphoryl ligand of lipopolysaccharide (Moat *et al.*, 2002). *Pseudomonas* species showed a good ability to resist and accumulate different metal ions namely Cr (VI), Cu (II), Cd (II) and Ni (II) from contaminated waste water (Hussein *et al.*, 2004). Among bacteria, *Bacillus subtilis* and *Pseudomonas aeruginosa* were efficient in metal sequestration and had been used in commercial biosorbent preparation (Tunalia *et al.*, 2006 and Lin and Lai, 2006).

Biosorption by fungi

The majority of fungi show filamentous or hyphal growth, they are easy to grow and yield large amount of biomass. Cell walls of fungi present a multilaminate architecture where upto 90% of their dry mass consists of amino or nonamino polysaccharides. The fungal cell wall can be considered as a two-phase system consisting of chitin framework embedded in an amorphous polysaccharide matrix (Talaro and Talaro, 2002). In filamentous fungi the outer cell wall layers mainly contain neural polysaccharides (glucans and mannans), while the inner layers contain more of glucosamines (chitin and chitosan) in

the micro fibrillar structure. Various metal binding groups, viz, amine, imidazole, phosphate, sulphydryl, sulphate and hydroxyl are present in the polymers (Deng and Ting, 2005).

The relative importance of each of these groups is difficult to resolve on the account of complexity of organization of cell wall, and different types of interactions with the metal ions occurring simultaneously (Sag, 2001). The metal binding capacity depends on the cell wall polymers as well as their alignment in the cell wall. Metal binding capacities in different fungi alter due to differences in their cell wall composition. Proteins are also found to be associated with metal binding activity (Paknikar *et al.*, 2003).

Many fungal isolates have shown an excellent potential of metal biosorption, particularly *Aspergillus niger, Aspergillus fumigatus, Aureobasidium pullulans, Cladosporium cladosporides, Fusarium oxysporum, F. moniliforme* and *Mucor hiemalis* (Pethkar and Paknikar, 1998). Sag *et al.* (2000) reported that *Rhizopus arrhizus* was able to remove lead, nickel and copper efficiently from aqueous metal solution. Sen *et al.* (2005) studied the biosorption of chromium by non living *Fusarium* species isolated from metal contaminated soil.

Biosorption by algae

Special polysaccharides are present in the algal cell wall. The number and kind of binding sites depend on the chemical composition of the cell wall. It has been suggested that the polysaccharides of cell could provide amino, carboxyl group, nitrogen and oxygen based moieties could also form coordinate bond with metal ions. Metal ions could also be electrostatically bonded to unprotonated carboxyl oxygen and sulphate. Covalent bonding

between divalent cation and algal cell wall proteins has also been reported. Additional mechanisms such as entrapment of metal both in the form of insoluble micro deposits in inter and intra fibrillar capillaries and paracrystalline regions of polysaccharides and the binding to other biopolymers (RNA, polyphosphates) can contribute to the metal binding (Vasudevan *et al.*, 2001 and Davis *et al.*, 2003).

Baran *et al.* (2005) reported the maximum sorption capacity of *Halimeda tuna, Sargassum vulgare, Pterocladia capillacea, Hypnea musciformis* and *Laurencia papillosa* for the removal of chromium from aqueous solution. Penche *et al.* (2005) studied the biosorption of copper, zinc, cadmium and nickel by *Chlorella vulgaris*.

In different species of the genera *Chlorella, Ulothrix, Chlamydomonas, Scenedesmus, Spirulina, Cyanidium* and *Sargassum* the ionic charges and covalent bonding were involved in metal binding (Kumar and Kaladharan, 2006).

Murphy *et al.* (2007) studied the biosorption efficiency of dried biomasses of the marine macroalgae, *Fucus uesiculosus* (brown), *Ulva lactuca* (green) and *Polysiphonia lanosa* (red) on copper removal.

2.4.1.2. Metabolism dependent biosorption

Metabolism dependent uptake of metal ion is usually a slower process than independent biosorption although greater amounts of metal may be accumulated by this means in some organisms, like yeast. Transport of metal ions into microbial cells is inhibited by low temperatures, metabolic inhibitors and absence of an energy source. Rates of uptake are influenced by the metabolic state of cells and the composition of the external medium (Gadd, 1990).

2.4.2. Biosorption based on the localization site of heavy metal

Based on the localization site of the metals, microorganisms interact with the metal and remove them either by extracellular accumulation / precipitation, cell surface sorption / binding and intracellular accumulation (Ilhan *et al.*, 2004).

2.5. IMPACT OF WATER POLLUTION ON PLANT GROWTH

Aggarwal *et al.* (1990) studied the effect of different concentrations of cadmium and nickel on the growth of wheat and pigeon pea. They observed that seed germination, seedling growth and chlorophyll contents showed an increasing trend at lower concentration and gradually decreased with increased concentrations of cadmium and nickel.

Srikanth and Reddy (1991) opined that the heavy metals detected in vegetables grown in urban sewage caused health hazards to consumers. High concentration of cadmium, zinc, nickel and selenium were detected in grass samples grown in urban sewage sludge.

Gautam and Bishnoi (1992) reported the effect of dairy effluent on the growth of wheat (*Triticum aestivum*) at different concentrations of effluent. Their results inferred that plants grown in 25% concentration of effluent recorded higher shoot and root length, fresh and dry weight when compared with higher concentrations.

Vijayrengan and Lakshmanachary (1993) reported that the germination percentage of *Vigna radiata* seeds decreased with increased concentrations of textile effluent. Effluent at low concentration enhanced the growth and dry weight of the seedlings

whereas higher concentration caused deleterious effects and also reduced the chlorophyll content of green gram seedlings.

Joshi *et al.* (1994) reported the effect of chromium on the growth and development of cow pea (*Vigna unguiculata*). They observed the reduction in shoot and root length, fresh and dry weight of the seedlings at higher concentrations of chromium.

Thamizhiniyan (1995) had undertaken an investigation to study the impact of biologically treated sugar mill effluent on germination, growth and biochemical contents of groundnut (*Arachis hypogea*) and paddy (*Oryza sativa*).

Rahman *et al.* (1996) found that nickel and cobalt at higher concentrations (200 and 400 ppm) were harmful for chick pea cultivation. They observed that seed germination, plant growth and biomass were adversely affected and the chlorophyll content was greatly reduced. These adverse impacts were reflected in the reduced yield of the plant.

Saravanan *et al.* (1997) studied the influence of cadmium on the germination and growth behaviour of *Arachis hypogea* and observed the reduction at higher concentrations.

Application of lead at low levels (200 - 400 mg/kg soil) increased the dry matter yield of green gram, cowpea and maize but decreased the yield of other crops (Singh, 1998).

Ponmurugan and Jayaseelan (1999) assessed the impact of fire work and dye effluent on the seedling growth of *Typha angustata.* The seedlings treated with higher concentrations of effluent showed a marked reduction in shoot, root morphology and phytomass when compared to control.

Sundaramoorthy *et al.* (2000) investigated the effect of fertilizer factory effluent on the growth of green gram *(Vigna radiata*), black gram (*Vigna mungo*), groundnut (*Arachis hypogea*), soya bean (*Glycine max*), paddy (*Oryza sativa*) and sorghum (*Sorghum bicolor*). They observed that the seeds treated with increased concentrations of effluent showed a gradual decline in the germination percentage, seedling growth and dry weight.

The presence of chromium, lead, copper, zinc and iron were detected in industrial effluents and their effects on different plant species were studied (Sivakumar *et al.*, 2001). The changes in their physiology were observed and recorded. A drastic reduction in total chlorophyll content, leaf area, number of leaves, shoot and root lengths, fresh and dry weights of the plant species were observed.

Veliappan *et al.* (2002) reported that aluminium and mercury at 100 mM concentrations affected the growth of *Vigna unguiculata, Vigna mungo, Vigna radiata, Macrotyloma uniflorum* and *Lablab purpureus.* Among these two, mercury was found to be more toxic than aluminium.

Jothimani and Elayarajan (2003) reported that the textile and dyeing effluent treated with fungal systems showed a maximum shoot and root lengths when compared with the effluent treated with chemicals and bacterial systems.

The effect of zinc at different concentrations on germination, seedling growth and biochemical contents of black gram were investigated by Pavadai *et al.* (2004). They reported that the growth and biochemical contents were increased at lower concentrations and there was a gradual decrease at higher concentrations of zinc.

Deepthi *et al.* (2005) assessed the toxic effect of Dichlorophenyltrichloroethane (DDT) on the germination of seeds such as *Brassica juncea* (Mustard), *Raphanus sativus* (Radish), *Phaseolus radiata* (Green gram), *Phaseolus vulgaris* (French beans), *Hibiscus esculentum* (Ladies finger), *Oryza sativa* (Paddy) and *Eleusine coracana* (Ragi). They reported a marked reduction in the germination of the seeds with increased DDT concentration.

Ganesh *et al.* (2006) studied the impact of different concentrations of chromium and cadmium on germination, growth and photosynthetic pigment response of soybean. There was a gradual retardation of germination, root and shoot lengths, fresh and dry weights, chlorophyll and carotenoid content with increase in concentration, whereas no germination was observed in 500 mg/l concentration of chromium and cadmium.

Vijayaragavan *et al.* (2007) carried out a study on the effect of cadmium on biochemical constituents in radish (*Raphanus sativus*). He observed a reduction in chlorophyll, carotenoid, total sugar, amino acids and protein contents due to cadmium toxicity at higher concentrations.

Paneerselvam *et al.* (2008) reported the effect of different concentrations of dairy effluent treated with Arbuscular Mycorrizhal fungi on the biochemical constituents of *Phaseolus trilobus* Ait. They observed that microbially treated dairy effluent was found to exhibit more activity than the untreated effluent.

Gupta *et al.* (2009) studied the effect of lead on the biochemical constituents of the leaves of *Alstonia scholaris, Cassia siamea, Tectona grandis* and *Pterospermum acerifolium*.

2.6. EFFECT OF INDUSTRIAL EFFLUENTS ON SOIL PARAMETERS

Raguveer and Sastry (1990) observed no significant changes in the pH, bulk density and exchange capacity of the soil treated with pulp and paper mill effluent where chillies and cotton were grown.

Singh *et al.* (1991) opined that significant change in soil pH was reflected in long term study but even small changes may have significant effect on the growth of plant and soil microbiota.

Kannan and Oblisami (1992) reported that the soil irrigated with paper and pulp mill effluent was found to have increased amount of pH, electrical conductivity, organic carbon, available nitrogen, potassium and phosphorus.

Application of sewage sludge, paper and dye effluents to green gram and maize plants grown soil showed a high load of inorganic nutrients and minerals which altered the soil composition and also cause deleterious effect to the crops and soil texture (Shanmugavel, 1993).

Palaniswami and Ramulu (1994) reported the increased pH, electrical conductivity, organic carbon, exchangeable cations, available phosphorus, potassium, micronutrients and enzyme activities in the soil irrigated with paper factory effluent.

Raza and Murthy (1995) stated that the physicochemical parameters of soil decreased when irrigated with effluents of tanneries, breweries and pharmaceuticals in Nacharam industrial area, Hyderabad. The continuous application of sewage made the soil saline and the physiological response of plants showed negative correlation with chlorides, sulphates and total salinity of soil.

Singaram (1996) studied the chemical properties of soil irrigated with tannery effluent and recorded that the concentration of chromium in soil was increased to an alarming extent with increased dilution.

Seema (1997) studied the effect of Mathura oil refinery on soil quality and irrigation with this effluent containing high phenols, tars, oil and grease, nitrogen, organic carbon resulted in alteration of soil physicochemical characters, which in turn rendered the soil a detrimental effect.

Investigations carried out by Vasu *et al.* (1998) to assess the accumulation of plant nutrients (macro and micro nutrients) and heavy metals in soils by the land adjoining few industrial establishments in Kochi (Kerala), indicated high salinity, high organic carbon and an increased amount of nitrogen and phosphorus in the soils. They also reported high values of DTPA extractable micronutrients such as zinc, copper, manganese and iron in the soil.

Pathak *et al.* (1999) suggested that the use of distillery effluent as a nitrogen source by obtaining a significantly high yield in sugar cane with 20 kg nitrogen through spent wash application.

Chhonkar *et al.* (2000) stated that the use of distillery effluents indicated a significant increase in electrical conductivity, organic carbon, cation-exchange capacity, available sodium, potassium and phosphorus in soils.

Sastry *et al.* (2001) reported that the bicycle manufacturing industry altered the soil texture, moisture content, electrical conductivity, organic carbon, available potassium and phosphorus. Concentrations of chromium and nickel exceeded the permissible limits and the presence of cyanide in the effluents affected the soil.

Aydinalp and Marinova (2002) determined the levels of zinc and iron in the Bursa soil of Turkey, which was found to be high due to the discharge of various effluents from the industries without treatment, thereby polluting the soil and water resources.

Dodor and Tabatabai (2003) examined the discharge of dairy industry effluent into the soil which increased the soil organic matter, total nitrogen and phosphorus contents.

Baskar *et al.* (2004) reported that the distillery effluent slightly changed the physicochemical properties of the soil. The pH, electrical conductivity, organic carbon and soluble salt contents of the post harvested soil increased from the initial level due to the application of increasing dose of the effluent.

Begum and Subburam (2005) reported that the levels of pH, electrical conductivity, organic carbon, cation exchange capacity and free $CaCO_3$ were found to be higher in different areas of soil contaminated with the textile dye, congo red in Coimbatore district.

Jalali (2006) studied the characteristics of sewage, industrial effluents and canal water used for irrigation and their effect on soil. The pH, electrical conductivity and organic carbon were found to be higher whereas the DTPA extractable Zn, Cu, Fe, Mn and nickel were within the permissible limits.

Nagaraju *et al.* (2007) reported that the discharge of sugarcane effluent on soil caused changes in their physicochemical properties. The pH, water holding capacity, electrical conductivity, organic carbon, total nitrogen and phosphorus were found to be increased when compared with the control soil which is free of pollutants.

The effect of dairy factory effluent on the soil properties was assessed by Nizammuddin *et al.* (2008). Their results showed

an increased pH, water holding capacity, electrical conductivity, organic carbon, total nitrogen and phosphorus in the effluent contaminated soil.

Vidyavathi *et al.* (2009) reported the effect of gold ore tailings on the fertility status of soil and its application resulted in greater accumulation of micronutrients in soil.

2.7. EFFECT OF POLLUTANTS ON THE BIOCHEMICAL CONSTITUENTS AND HISTOLOGY OF FISHES

Awari and Gaikwad (1990) observed a gradual decline in the carbohydrate content of the fish, *Ambassis ranga* exposed to the heavy metal cadmium. Effect of lethal lindane and atrophine sulphate on the digestive tissues of the air breathing fish, *Anabas testudineus* was studied by Bakthavathsalam and Rajaretnam (1990).

James *et al.* (1991) observed a significant decrease in the protein, carbohydrate and lipid content in the muscle, liver and gill of *Oreochromis mossambicus* exposed to different metals individually and in combinations. Arsenic induced liver hyperplasia and kidney fibrosis was noticed by Kotsanis and Georgudaki (1991) in the *Oncorhynchus mykiss* (Rainbow trout).

Sen *et al.* (1992) studied the toxic effect of zinc on the brain and liver of *Channa punctatus* by increasing the exposure period from 30 to 75 days. There was a depletion of the total cholesterol, protein and ascorbic acid contents in the liver and brain as the exposure days increased. Histological changes of *Sarotherodon mossambicus* in gill structure under sublethal exposure to pesticides, DDT, BHC and endosulfan was observed by Ramalingam *et al.* (1992).

Ghosh and Konar (1993) assessed the effect of different concentrations of sugar mill effluent on the protein content of *Channa punctatus* in which they observed a significant decrease of protein content in the liver of the fishes. Jain and Mishra (1993) reported the herbicide induced histopathological lesions in the kidney of fish *Puntius stigma* which include hypertrophy and necrosis of kidney tubules and degeneration of haemopoietic tissues.

Ayyadurai *et al.* (1994) studied the impact of heavy metal pollution in the finfish, *Oreochromis mossambicus*. It was observed that maximum accumulation of metals such as copper, iron, manganese and zinc occurred in the liver rather than muscles, gills and viscera of the fish. Sakthivel (1994) reported the sublethal effects of tannery and textile effluent on the histopathological lesions of the gill structure of *Cyprinus carpio*.

Palanichamy and Baskaran (1995) studied the selected biochemical and physiological parameters of the fish *Channa striatus* to assess the heavy metal pollution in fresh water environment. There was a gradual decline in the protein and carbohydrate level when exposed to metals like mercury, cadmium and lead over a period of 21 days. Christy (1995) observed histological impairment in the gills of *Catla catla* exposed to sublethal concentrations of chromium.

Shakoori *et al.* (1996) studied the effect of fenvalarate in the fresh water fish *Etenopharyngodon idella* which showed a decline of protein and carbohydrate levels in muscle, liver and gills of the fishes exposed to higher concentrations. Dwivedi and Sarin (1996) investigated the histopathological changes in the liver of the cat fish, *Heteropneustes fossilis* induced by tri-aromatic hydrocarbon.

Sastry *et al.* (1997) reported the toxic effects of cadmium and copper individually and in their combination on the enzymological and biochemical parameters of the fresh water fish, *Channa punctatus.* Anithakumari and Kumar (1997) assessed the histological damage caused to the fish, *Channa punctatus* by various aquatic pollutants present in polluted waters of Hussein sagar.

Baruah *et al.* (1998) studied the toxicological effect of paper mill effluent on the muscle glycogen profile of *Heteropneustes fossilis* (Bloch), in which there was a significant decline in the glycogen content in the muscle tissues. Iyyappan *et al.* (1998) observed histopathological changes in vital organs namely gills, liver, kidney and spleen of the fish, *Etroplus suratensis* (Pearl spot) inhabiting the polluted waters of Uppanar estuary.

Virk and Sharma (1999) examined the biochemical changes induced by nickel and chromium in the liver of *Cyprinus carpio* exposed to 60 days. When compared to control the biochemical constitutents such as proteins, lipids, cholesterol and phospholipids of the liver were significantly reduced in the fishes treated with heavy metals. Balasubramanian *et al.* (1999) noticed changes in the liver and gill tissues of *Oreochromis mossambicus* under ambient urea stress.

Nanda *et al.* (2000) observed a significant decline in the protein level of liver, muscle and gills of *Heteropneustes fossilis* exposed to nickel for 30, 60 and 90 days. Kumar (2000) observed histopathological changes in the liver of a fresh water fish, *Channa punctatus* exposed to chronic levels of ammonia. Effect of carbamate (Furadan - 3G) on the histopathological changes in the gills of *Channa marulius* was studied by Prasad *et al.* (2000).

The impact of distillery effluent on the biochemical contents (proteins, carbohydrates and lipids) of the fresh water teleost, *Channa punctatus* was studied (Kumar and Gopal, 2001). A gradual decline in the biochemical contents of the liver, muscle and gills of the fishes. Tilak *et al.* (2001) studied the histopathological changes in the gills, liver and kidney of *Ctenopharynogodon idellus* (valenciennes) exposed to fenvalerate and EC.

Desai *et al.* (2002) observed the effect of nickel on the fresh water fish, *Channa punctatus* which was exposed to nickel at different concentrations. As the concentrations of nickel increased there was a gradual decline in the protein content of the liver tissues. Adewoyo and Fawole (2002) studied the acute toxicity of soap and detergent effluents on the histopathology of *Clarias gariepinus*.

Vutukuru (2003) observed chromium induced alterations in the biochemical constituents of *Labeo rohita* (Ham.). There was a significant decline in the carbohydrate and protein content of the fishes exposed to chromium.

Sonawane *et al.* (2004) observed a sudden depletion in the glycogen, protein and free amino acid contents in the tissues of the fish *Lepidocephalus thermalis* exposed to different concentrations of sugar factory effluent. Pallavi and Neera (2004) noted the histological changes in the kidney of the fresh water fish, *Channa punctatus* exposed to sublethal concentrations of zinc.

Revathi *et al.* (2005) studied the effect of tannery effluent on the larvivorous fish, *Gambusia affinis.* They observed a significant decrease in the protein level of muscle, gills and liver tissues. Manisha and Dhande (2005) studied the ultra structural changes in

the gill lamellae of fresh water major carp, *Labeo rohita* exposed to sublethal concentrations of copper sulphate.

Venkataraman *et al.* (2006) studied the impact of malathion on the biochemical constituents of gobid fish, *Glossogobius giurius* (Ham.). They observed a gradual decline in the protein and carbohydrate contents. Athikesavan *et al.* (2006) observed the effect of histopathological changes in the gills, liver, intestine and kidney of the fresh water fish *Hypophthalmichthys molitrix* exposed to nickel.

Kaur and Virk (2007) observed the changes in the protein content of the muscles and gills of *Cyprinus carpio* exposed to nickel and chromium. The protein content in the muscle and gills of the fish were found to be declined which may be due to the interference of heavy metals in protein synthesis. Rani and Raju (2007) investigated the histopathological variations in the tissues such as liver, kidney and gills of fresh water teleost, *Tilapia mossambica* (Peters) exposed to sublethal concentrations of arsenic.

Subramanian *et al.* (2008) studied the effect of lead acetate on protein metabolism of the fresh water fish, *Oreochromis mossambicus.* Fishes exposed to lead acetate were found to have a significant decline in the protein level of liver tissues. Sornaraj *et al.* (2008) studied the histopathological alterations in the architecture of stomach of the fish *Mystus vittatus* reared in the pesticide mixed medium.

Ogundiran *et al.* (2009) investigated the pathologic lesions in the gills of *Clarias gariepinus* exposed to sublethal concentrations of soap and detergent effluents.