CHAPTER 2

REVIEW OF LITERATURE

2.1 HEAVY METAL POLLUTION

The concentration of toxic heavy metals is continuously increasing in our environment and has become significant after an intensive industrial development. Modern civilization is now dependent on the large-scale use of a wide range of metals and most of these are naturally occurring only at the trace levels in the biosphere. When a living organism absorbs a potentially toxic metal at abnormally high concentrations, it may cause structural damage of enter cells and inhibit enzyme activities to such an extent that the normal cell functioning is impaired.

Heavy metals continue to be of major environmental concern due to their toxicity to human and other living organisms. Major inputs of metals are from the electroplating and metal finishing practices (Peters and Ku 1987). The rapid pace of overall industrial progress in the past few decades has brought astonishing growth of electroplating industries because of the requirements of low cost metal surfaces which can withstand hostile environments in various industrial sectors where surface finish, luster and aesthetics are of prime importance (Kumar et al 1993). Discharge of effluents from industries without proper treatment has posed a threat to human health from heavy metals.
2.2 SOURCES OF HEAVY METAL POLLUTION

Heavy metals find their way into the water cycle by the following sources.

i) Natural processes such as corrosion, weathering of rocks, volcanic activity etc. and

ii) Anthropogenic sources, which include either direct addition through industrial and agricultural practices or indirectly through the atmospheric precipitation of industrial pollutants and automobile emissions with subsequent storm water wash.

2.2.1 Geological Weathering

Geological weathering is an important source of base line background metal levels. In areas with metal bearing rock formations, high levels of heavy metals are likely to occur in water and bottom sediments. The accumulation of cadmium, manganese, nickel and zinc in water and bottom sediments of river Ganga has been studied for the 480 km stretch from Badrinath to Narora and appears to remain below toxic limits. As this stretch is relatively free from human activities, the incidence of heavy metals may be attributed due to the geological sources (Saikia et al 1988). Arsenic-rich hot springs arising from geothermal activity feed the Waikato river of North Island, New Zealand. Submerged aquatic plants in this river were found to contain a maximum of 650 mg of arsenic per kg of dry mass as compared to levels below 12 mg/kg in plants growing in natural soils (Forstner and Wittmann 1983).
2.2.2 Mining Effluents

Some of the sources that produce serious pollution of acidic water are from mine pits, waste rock dump and surface water that may be contaminated around handling facilities. Mines of the Philippines were found to add substantial amounts of heavy metals such as mercury and nickel to the nearby rivers (Leland et al. 1978). Erosion and leaching of abandoned deposits of lead mine tailings in south-east Missouri have resulted in the heavy metal contamination of surface waters, sediments and aquatic biota. The results indicated that leachates from mine tailing deposits can adversely affect aquatic invertebrates (Besser and Rabeni 1987). The wastewater from Brunswick mine with a pH of 3.0 contained 389 ppm of zinc, 31 ppm of copper and 131 ppm of iron (Forstner and Wittmann 1983). A preliminary study of chemical characteristics of wastewater habitats of Zawar mines, Udaipur revealed the presence of high concentrations of Cd, Cu, Pb and Zn (Rana et al. 1971).

Changes in the pH of the Guadiamar River, following the re-opening of a pyrite mine, were studied. A decrease in pH of the river water increased the solubility of heavy metals of soils of the river bank causing an increase in the amount of these metals transported into the Donana National Park, Spain. Under acidic conditions, more Cd, Hg and Zn migrated than Cu and Pb (Gonzalez et al. 1990).

A survey to assess the impact of mining of galena, sphalerite, chalcopyrite and pyrite between 1945 and 1985 was made in Gyongyosoroszi, Hungary. The survey covered sampling, analysis and data evaluation of waste materials, soils from several parts of the village, water samples from the brooks and lakes, sediments from the water bodies and plants growing in home gardens.
exponentially with distance from the mine source, mainly due to dispersion by water and topography (Jungmyungchae et al 1996).

A study was prompted by concern about the possible heavy metal contamination of the Flumendosa lake, a drinking water reservoir located downstream from a mining area in Sardinia (Italy). Extremely high concentrations of Cd, Cu and Pb were found in a small tributary of the Flumendosa river which drains the mining areas. Sediment cores from the reservoir showed high contents of all three metals (Schintu et al 1991).

A tri-state mining region, including parts of Missouri, Oklahoma and Kansas was the site of intense lead and zinc mining and smelting activity until the 1950s. A study was initiated to characterize the heavy metal contamination of soils in this area (Saheb et al 1994). The concentration ranges in soil samples were 15 - 86 mg/kg Cd, 35 - 1620 mg/kg Pb, and 99 - 18500 mg/kg Zn.

The concentration of Cu, Ni, Zn, Fe, Mn, Co, Pb and Cr in water and sediment were high in a reservoir located in Daitari iron ore mining area of Orissa, India. The aquatic plants have bio-accumulated these heavy metals (Panda et al 1996). In mining areas, the run-off water and discharge of effluents to the surrounding places have polluted the nearby aquatic ecosystems. A few reports are available on the distribution of heavy metals among biotic and abiotic components of aquatic ecosystems of mining areas (Brooks et al 1982, Bubicz et al 1982, Joshi et al 1982 and Tam 1977).

Reddy and Singh (1994) assessed the heavy metal concentration from groundwater of Dhanbad City and raised doubts about the potability of these
Chromium, copper, manganese, iron, nickel, silver and zinc were present at significant concentration in many samples.

### 2.2.3 Domestic Wastewater

The sewage generation from urban centers in India grew from 5 billion litres a day in 1947 to 30 billion a day in 1997 (Lark et al. 2002). The available treatment capacity of 3 billion litres a day is just 10% of the total wastewater generation. Out of 3119 cities in India only 8 cities are provided with the treatment plants. Consequently in most of the A class cities, disposal of sewage is carried out by using it for irrigation. This kind of land application of the municipal sewage results in direct addition of trace metals to the soil resulting in its degradation and also adding toxic metals in the food chain (Lark et al. 2002).

Domestic sewage has a marked influence on the concentrations of cadmium, copper, lead, silver and zinc. All these metals, except silver, may be present due to corrosion of water supply network. The use of detergents also created a possible pollution, as the common household detergents affect water quality. A study regarding the relative contribution of heavy metals to the New York City wastewater treatment plants showed that domestic or residential sources predominate for cadmium, copper and zinc input because of corrosion within water supply system (Hart 1982). The use of detergents also adds to heavy metal pollution. Trace amounts of chromium, cobalt, iron, manganese and zinc were found in most enzyme detergents (Forstner and Wittmann 1983).

An analysis of 15 samples collected from different locations in the Kolkata metropolitan area revealed the presence of significant amounts of chromium, cobalt, copper, lead, manganese, nickel and zinc (Bhowal et al. 1987).
Dlaniya et al (1998) studied the effect of heavy metal pollution on vegetation due to the application of municipal solid waste in Kolkata. This study reveals the extent of contamination of soil and vegetation due to the application of municipal solid waste on agricultural land.

Total and extractable heavy metal contents of sewage from Mumfordganj, Allahabad, India, were determined by atomic absorption spectrophotometry. In sewage samples, the cadmium content was 0.26-0.85 mg/L which is higher than the FAO maximum permissible level for irrigation water (0.01 mg/L). The lead content was 0.7-5.8 mg/L (FAO limit for irrigation water 5 mg/L). The zinc, iron and manganese content were 5.8-10.0, 8.0-12.0 and 10.6-13.6 mg/L, respectively (Irrigation limits are 32, 5 and 0.2 mg/L, respectively). The heavy metal levels in sewage were lower than those found in industrial effluents but were high enough to be toxic to crops (Misra and Mani 1992).

Surface soil samples were collected from the field along a sewage drain (in Armitasar, India) which were irrigated with sewage effluent, sewage effluent mixed with tube well water or tube well water alone, and their chemical characteristics were investigated. Results showed that irrigation with sewage effluent mixed with tube well water significantly decreased soil pH and increased electrical conductivity and organic matter content. Zn and Cu contents increased 3 and 8 fold, respectively in the sewage effluent irrigated soils, reaching levels toxic to plants (Hundal and Sandhu 1990).

Dwivedi and Tiwari (1997) reported that Ganga river at Varanasi, India is polluted with heavy metals such as cadmium, chromium, copper...
manganese and zinc mainly due to the discharge of untreated sewage from the City of Varanasi.

The study on Shahpura lake, Bhopal (Saxena et al 1998) revealed contamination by sewage, heavy metals such as Cd, Cr, Pb, Ni and Zn beyond the surface water quality limits. High concentration of metals was also observed in the plankton and fish muscles.

2.2.4 Industrial Effluents

There are numerous industrial activities leading to heavy metal enrichment of the aquatic environment. Major trace elements generally present in various industrial effluents are listed in Table 1.2. The characteristics of various industrial wastewaters may also vary considerably both in quality and quantity. Metals in the wastewater may occur in forms ranging from particles of pure metals in suspension to metal ions and complexes in solution. Pollutants from electroplating operations can find their environmental pathways through air, food materials, soil and water into plant and animal tissues. Metals tend to get adsorbed easily on surfaces of soil or sediments.

Spatial and seasonal variations in metal concentrations of Skeleton Creek, Oklahoma, showed evidence of contamination due to industrial and domestic effluents by increased concentrations of Cr, Cu, Pb and Zn (Leland et al 1978). Gold mining industries located at eastern slopes of Black Hills of South Dakota have used metallic mercury for extraction of gold from pulverized ores, the liquid wastes of which containing mercury found their way into Missouri river (Walker et al 1974). In a study, cadmium and nickel enrichment were found in an aquatic system in the marshes and coves along the
Urbanization and industrialization, especially the battery manufacturing units on the banks of the Adyar river are the strong sources of lead contamination of sediments in the Chennai coast (Ramani and Kumar 1997). The automobile exhaust is also suspected as a significant source of lead (Sundari 1991) in the study area.

The wash water from plating operations in a surgical instruments factory, Adyar, Chennai containing excessive amounts of hexavalent chromium and nickel were sent to sewers (Sreenivasan et al 1971). Levels of Cd, Cr, Cu, Pb, Hg, Ni and Zn in water and sediment from the mouth, centre and upstream area of the Ennore and Adyar estuaries and Lake Pulicat near Chennai, Tamil Nadu, India were measured over a year. The samples from the lake contained only traces of heavy metals. Water samples from the Adyar estuary contained more Pb than those from the Ennore estuary due to limited dry season flow in the Adyar. The sediment heavy metal levels in Ennore increased upstream while that in Adyar increased downstream. Adyar sediment heavy metal levels were maximum during low flow conditions in May (summer). Ennore sediment heavy metal levels were maximum during the monsoon season in November, as a result of run off from the disposal sites of petrochemical plants (Joseph and Srivasta 1993).

Cadmium, chromium, lead and manganese have been found in four varieties of Portland cement manufactured in India. A survey has shown...
enhanced urinary excretions of manganese and lead in majority of cement workers (Tandon et al 1984).

Industrial and municipal wastewaters were directly discharged to rivers in Hanoi, Vietnam. Sediments were collected from different sites of three rivers in the industrialized and densely populated area of Hanoi City and examined for total heavy metals and metal fractions using sequential extraction procedure. Concentration of the total heavy metals ranged from the background levels to above the maximum permissible levels for crop growth. Total concentration of heavy metals varied from site to site and tended to be high in the site where manufacturing companies were located (Thilamtraho and Egashira 2000).

Studies on the status of pollution caused by steel plant wastes in river Damodar revealed less number of organisms indicating a stressful habitat causing degradation (Chakraborty and Konar 2002).

Investigations were carried out by Vasu et al (1998) to assess the accumulation of plant nutrients and heavy metals in soils of the lands adjoining few industrial establishments in Kochi, Kerala. The studies indicated high salinity, organic carbon and enrichment of major nutrients like nitrogen and phosphorus in the soil. High levels of micronutrients such as zinc, copper, manganese and iron were also observed in the soils.

The Ramaganga river, Moradabad was polluted with heavy metals such as Cd, Cu, Fe, Pb, Ni and Zn by brass factories, stainless steel plants, electroplating units, etc. (Pande and Sharma 1999).
An environmental impact assessment of tannery effluents on heavy metal phytotoxicity and health hazards was carried out by Sharma et al (1996). The crops irrigated with tannery effluents showed accumulation of heavy metals. Consumption of these crops lead to physiological disorders and carcinogenicity in man and cattle.

2.2.5 Atmospheric Sources

Metals are released to the atmosphere in the form of air-borne particulates by both natural and manmade processes. Nonferrous metal production, combustion of gasoline and diesel mainly account for heavy metals like cadmium, lead, nickel and zinc.

Most of the metals in the atmospheric environment were in the form of oxides. These were removed by precipitation with rain or by gravitational fall out (Leland et al 1978). A forest catchment area in the vicinity of two coal-fired power plants received rainfall containing trace metals in concentrations quite typical of rural areas (Leland et al 1978). Concentrations of Cu, Co, Ni, Pb, Zn, Bi and Sb were determined in the flyash samples collected in the vicinity of thermal power plant. The permeabilities of these elements also determined the soil horizon (Patel and Pandya 1987). Exhaust air from zinc mines at Zawar in Udaipur contained high concentrations of As and Pb. Deposited dust near the exhaust fan site showed high concentrations of cadmium (Gopalakrishnan et al 1984). South east Tennessee’s copper basin and the Konnet area of northern California were notable examples for smelter smoke which has killed vegetation and poisoned the soil around smelters (Bullard 1966).
Heavy metal contamination of natural soils due to atmospheric transport in the northern part of Eastern Carpathians was studied in an area north of Baia Mare, the main Romanian centre for processing complex sulphide ores. The distribution of Cd, Cr, Co, Cu, Pb, Mn, Ni and Zn was studied along the soil profile and at specific distances from the pollution sources (Donisa et al 2000).

Natural surface soils in Southern Norway were highly contaminated by metals from atmospheric deposition. Except from local pollution with Cu, Ni and to a limited extent Pb around the town of Kristiansand, this large-scale contamination can be ascribed to long-range atmospheric transport from other parts of Europe. As, Cu, Pb and Zn were found in excessive concentrations in the surface layer of natural soils throughout the region, and in particular within a zone of about 20 - 40 km from the coast (Steinnes et al 1989).

### 2.2.6 Agricultural Sources

Agriculture constitutes one of the most important non-point sources of metal pollutants (Alloway and Ayres 1997). The main sources are:

(i) Fertilizers: Cd, Cr, Mo, Pb, U, V, Zn and
(ii) Pesticides: Cu, As, Hg, Pb, Mn, Zn

The heavy metal ions contribution to foodstuffs through soil-plant-animal chain bears close scrutiny. Crop plants absorbed and accumulated toxic amounts of these metals and resulted severe health problems to humans and animals (Cook 1977 and Shrivastava et al 1989).
Soil may become enriched with hazardous heavy metals by the application of plant nutrients and crop protective measures. Rock phosphates and phosphatic fertilizers contain high levels of trace elements, especially cadmium. Sewage sludge applied to agricultural land contains trace elements in toxic proportions. Upon decomposition of sludge these elements are released and become available for plant uptake. An important bird feeding ground in Eastern England has been threatened by mercury pollution, probably caused by the use of mercury fungicides (Leland et al 1978). Irrigated agriculture involves leaching of materials from soil. Heavy irrigation is often used, specifically for flushing from the soil unwanted salts that inhibit crop growth (Bullard 1966).

2.2.7 Urban Storm Water Run Off

Urban storm water is considered as one of the major polluting sources. The storm water discharges and combined sewage overflows from urban areas create problems of ever increasing importance. The first flush carries very high load. Dust fall in New York City was contributing approximately 20% of the toxic heavy metals transported to the harbor by run off (Leland et al 1978). Little Custer lake in Indiana received large inputs of Cd, Cr, Pb and Zn from urban run off and industrial discharge, and the pollution was reflected in above normal concentrations of the elements in water, sediments and fish (Leland et al 1978). Snow from roads was shown to contain substantial amounts of Pb from combustion of leaded gasoline (Leland et al 1974). An investigation conducted at Gothenberg, Sweden revealed that corrosion of copper and zinc roof fittings was an important contributory source towards enrichment of these metals in urban storm water run off (Forstner and Wittmann 1983).
The pollution of urban soils and communal wastewater by traffic-induced heavy metals was studied at a dual carriage way near Giessen (Germany). Surface run off was collected hourly using a sampler installed in a storm drain. The concentration of heavy metals in the run off water was maximum at the beginning of a rainfall period. The duration of the dry period between rainfall events had a significant effect on the heavy metal content of the run off (Gath and Frede 1990).

Preliminary investigations carried out on the floodplains of the polluted Elbe river, Germany showed that the high flood sediments and soils of the flooded areas were contaminated with heavy metals (Meissner et al 1994).

Studies of Lee and Tounay (1998) on soil collected from motorways in Sologne showed that the soil was polluted with Cd, Fe, Pb, Mn and Zn. The relative mobility of heavy metals was found to be Mn = Cd>Zn>Pb>Fe.

2.3 EFFECTS OF HEAVY METALS

Some of the heavy metals, despite their usefulness when present in very small quantities, turn out to be hazardous if their concentrations increase beyond the permissible levels. Several of these heavy metals are bio-accumulative and detrimental to human health (Rai et al 1998). Exposure to toxic metals could occur through inhalation, ingestion and dermal contacts. The toxic elements discharged into the effluents will be absorbed and accumulated by microorganisms. Eventually, the toxic elements will get transferred to humans via the food chain (Cheung et al 2001). The toxic heavy metals entering the ecosystem may lead to geoaccumulation, bioaccumulation and biomagnification (Olaniya et al 1998). Outbreak of Itai-Itai (Ouch ouch) disease...
among Japan farmers due to the use of cadmium bearing Jintsu river water and Minamata disease due to the bioaccumulation of mercury in human body through food chain, particularly through fish, is the classic example (Rai et al 1998).

2.3.1 Effects of Heavy Metals on Human Health

Trace quantities of certain elements have some influence on living organisms. However, more recently great interest has been envisaged on the specific role of these elements. Certain heavy metals present at trace amounts in human tissues are essential to health and others have no apparent physiological functions. From the health point of view the metals can be grouped as follows (Ramachandran 1980):

i) Metals which are essential to life processes such as Cr, Co, Cu, Fe, Mn, Zn, etc.

ii) Metals which are probably inert to living systems such as Ba, Al, Li, etc.

iii) Metals which are slightly toxic to life processes such as Sn, As, etc.

iv) Metals which are highly toxic to life such as Cd, Pb, Hg, etc.

Even though some heavy metals are essential to the living system, they cause direct toxicity to both humans and other living beings due to their presence beyond specified limits. Toxic effects of heavy metals on human beings are given in Table 1.5.
Heavy metals not only cause phytotoxicity (Silverberg 1976 and Saxena et al 1991) but also enter into the food chain resulting toxicity in animals and may be carcinogenic to man (Bowen 1966, Chandra 1988, Friberg et al 1974, Kjellstrom et al 1979 and Sittig 1980).

The problem of heavy metal contamination in relation to human health is viewed in the light of anthropogenic developments in general. There is need to monitor agricultural products, air and water, establish territorial characteristics and rectify imbalances in microelements are pointed out. Attention is drawn to specific features of Cd pollution, human pathological effects resulting from heavy metal imbalances as exemplified by Zn and other microelements, regional excesses or deficits, and changes in mineral substances noted as occurring in association with various diseases (Yagodin 1995).

Presence of certain metals in the environment is hazardous in one way or another to humans and/or to other forms of life. The hazard to human may be in the form of acute or chronic toxicity, or the metal may act in more subtle ways causing cancer and other secondary effect diseases or damage to foetus. Aquatic organisms in fresh water or marine environment are often extremely sensitive to even very low concentration of metals. Metals in soil and irrigation water may adversely affect plant growth and mammals may also be affected both through the food chain and by contaminated drinking water (Conner 1990).

The study of Bihari et al (2001) on the health hazards among brassware workers in Moradabad showed that chronic bronchitis was prevalent among moulders while bronchial asthma was found to be more prevalent among welders. During manufacturing, these workers are exposed to a variety
of pollutants in the form of metal fumes, fine metal dust of chromium, copper, iron, nickel, zinc, etc, coal dust, smoke, corrosive acids, caustic alkaline solutions and solvents which are known to produce respiratory, allergic and dermatal hazards (Young 1965, McConnell et al 1973 and ILO 1998). The increased prevalence of bronchial asthma in welders in comparison to control subjects might be due to exposure to nickel which is a known allergen (McConnell et al 1973, ILO 1998, Dolovich et al 1984, Novey et al 1983 and Srirakawa et al 1990). The workers live and work in the same environment and hence the risk of health hazards to the workers is enhanced.

Clerk et al (1984), Srivastava et al (1988b) and Rastogi et al (1991a) reported that the chronic occupational exposure to even low doses of metals may be responsible for respiratory morbidity in glass bangle industries. Similar findings have been reported earlier on children exposed to multimetals in the brassware industry (Bihari et al 1992 and Anand et al 2000). Respiratory diseases were the most common cause of sickness among these workers.

Clerk et al (1986) reported that in the agate industry the workers were exposed to high concentration of free silica during grinding of agate stones, while in glass bangle and brassware industries, besides exposure to metal fumes, the workers were also exposed to coal dust and smoke from burning of coal. Occupational exposure to welding fumes and gases has been reported to be associated with prevalence of respiratory symptoms and pulmonary functional abnormalities (Kilburn et al 1990 and Rastogi et al 1991b). These studies signify the role of environmental pollution caused by the brassware industries as a whole (Srivastava et al 1988a and Rastogi et al 1989). Increased prevalence of chronic bronchitis has been reported among glass bangle workers and arc welders (Mathur 1965, Srivastava et al 1988b and Poika et al 1977).
2.3.2 Effects of Heavy Metals on Plants and Animals

The wide occurrence and the distribution of the trace elements in the soils, plants and animals have been adequately documented by Allaway (1968), Antonovics et al (1971) and Berrow and Webber (1972). Each toxic metal when ingested has a target tissue or tissues, causing specific ailments if taken more than the stipulated limits. Prolonged intake of heavy metal contaminated vegetables leads to diseases connected with lungs, heart and skin (Bowen 1979).

When plants grow on polluted soil, they accumulate high quantities of metals leading to their abnormal physiological behaviour. Copper easily affects seed germination. Copper applications in the form of CuCl$_2$ . 2H$_2$O inhibits nitrogen fixation in the case of soybeans. Nodule number, dry weight and nitrogen fixation were all inhibited (Alloway and Ayres 1997).

Lead has significant effect over the physiological function of plants life such as photosynthesis and transpiration. Due to lead elongation of seedlings’ chlorophyll content were affected in rice plant. Cr, Cu and Hg tolerance of four pasture plants during germination stage was studied (Maury et al 1986). The relative order of the metal toxicity was Hg>Cu>Cr. Copper was found to be concentrated more in the rootlets of plants. There was no detectable Cd concentration.

Toxicity of heavy metals retards plant growth and development, and damages the enzyme and stomatal activities and photosynthesis of plants causing a decrease in plant nutrient uptake and yield (Yagdi et al 2000).
The acute toxicity of Cd, Cu and Zn to the water flea, *Moina irrascens*, was evaluated and the degree of toxicity followed the order Cu>Cd>Zn. Modification of heavy metal toxicity by adjusting the environmental variables such as pH and temperature was also considered. It was demonstrated that pH had a significant effect, with metal toxicity at acidic pH being generally higher than at a basic pH. Increase in temperature in the range 20-30°C generally enhanced the metal toxicity (Zou and Bu 1994).

Singh et al (1996) reported that the discharge of highly toxic effluents from electroplating effluents directly or indirectly into sewers, natural drains or rivers disturbed the aquatic life and created an ecological imbalance. Moreover, the existence of useful microbes was endangered. Short term (acute) toxicity of these metals was of major concern previously but their slow accumulation in the physiological system of living beings through food chain (Grimji 1993) and their inherent chemical stability and nonbiodegradability (Tarzwell 1958 and Tarzwell 1971) have given way to great interest in their long term (chronic) consequences since in ecological terms disturbed behaviour, impaired physiology or induced sterility can have more or less the same ultimate effect on population or organism as the fairly rapid death of individuals. Nigam et al (1998) studied the bio-magnification of heavy metals in aquatic biota of a lake in Lucknow, India.

### 2.3.3 Effects of Heavy Metals on Biological Treatment

Most of the heavy metals are toxic to microorganisms. This is important while considering the biological treatment of wastewater. So, they need special attention in the design of treatment plants. Presence of heavy metals may lead to the malfunctioning of treatment plants. Copper is toxic for
sludge digestion at a concentration of 500mg/L. Due consideration should be
given to chromates and cyanides while industrial effluents mix with the
municipal wastewater.

Ali and Deepak (1996) studied the effect of mercury on aerobic biological treatment process. Mercury at low concentration had little effect on
the mixed culture biomass; however, high dosages had bacteriostasis effect.
This effect increased with increase in mercury concentration. The time required
for acclimatization increased with increase in mercury dosage.

2.4 METHODS OF HEAVY METAL REMOVAL

Due to problems associated with heavy metals pollution, much
importance has been given to the removal technology exclusively in wastewater
treatment. They are to be removed from wastewater in order to meet the
standards prescribed by pollution control boards so as to preserve the
environment. It is therefore necessary to exploit the best possible method by
which the metals can be removed effectively. Many techniques have been
developed to control the sources of heavy metals and improve their recovery.

Wastes containing heavy metals are extremely pernicious due to the
fact that they are environmentally persistent and toxic. Heavy metals are
generally refractories and cannot be degraded or detoxified biologically
(Srivastava et al 1996). Hence, it is a challenging task for the industries to
dispose these wastes in a safe and effective manner. Various techniques
developed for the removal of heavy metals include chemical precipitation, ion
exchange, reverse osmosis, electro-dialysis, absorption and adsorption (Manji
and Anirudhan 1990).
2.4.1 Chemical Precipitation

Chemical precipitation is the most commonly employed and simple technique for the reduction of metal concentration in wastewater (Archana and Shukla 1994). It is the treatment process most often employed to remove heavy metals from metal finishing waste streams. This method is used by approximately 75% of the electroplating facilities that generate aqueous metal-bearing wastes (Chhatwal 1997). It is a simple and economical method and, hence, has been widely used (Tokunaga et al 1999).

Chemical precipitation is applicable to the treatment of aqueous hazardous wastes containing toxic constituents that can be converted into an insoluble form. This is a direct application of the solubility product principle. The solubility product values of metal sulphides, hydroxides and carbonates (Jancuk and Fisher 1995) are provided in Table 2.1.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Ksp</th>
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<tbody>
<tr>
<td></td>
<td>Sulphide</td>
</tr>
<tr>
<td>Cadmium</td>
<td>1.4 x 10^{-29}</td>
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<tr>
<td>Chromium</td>
<td>-</td>
</tr>
<tr>
<td>Copper</td>
<td>2.8 x 10^{-45}</td>
</tr>
<tr>
<td>Lead</td>
<td>9.1 x 10^{-29}</td>
</tr>
<tr>
<td>Nickel</td>
<td>1.1 x 10^{-21}</td>
</tr>
<tr>
<td>Zinc</td>
<td>2.9 x 10^{-25}</td>
</tr>
</tbody>
</table>
The heavy metal ions present in aqueous medium can react with appropriate anions to generate insoluble precipitates. The precipitated metals can be removed by settling or filtration. It offers a high efficiency in the removal of heavy metals (Jorgensen and Johnsen 1981).

Metal removal techniques currently practiced on aqueous wastes include hydroxide, sulphide and carbonate precipitation processes (Larry et al 1982 and Chhatwal 1997).

2.4.1.1 Hydroxide precipitation

Traditionally, dissolved metals have been removed from water by hydroxide precipitation. It is widely used in treating aqueous metal waste streams. This technology offers an effective and economical method for removing heavy metals from spent process wastewaters. The most common precipitating agents used include calcium hydroxide (lime) and sodium hydroxide (caustic soda).

Lime is the most economical and common reagent used for the precipitation of metals from aqueous wastewaters. The process converts soluble metal ions into sparingly soluble metal hydroxides which can be separated from the supernatant by sedimentation and /or filtration. Since the minimum solubility of different metal ions corresponds to different pH, treatment of mixed-metal aqueous wastes may require some degree of adjustment. Typically, the optimum pH for hydroxide precipitation is between 9.5 and 11 (Chhatwal 1997).
Another problem associated with this process are that the reactions are of an equilibrium type, i.e., some metal hydroxides may dissociate leading to the metal ions going back into solution. For example, nickel and chromium have their lowest solubility at pH 10.5 - 11.0, and 7.5 - 8.0, respectively. Therefore, this method of metal removal may leave high levels of some metals still in solution or require an additional pH adjustment step. Further, mercury cannot be removed by this method.

Disadvantages encountered while resorting to hydroxide precipitation are: voluminous sludge production which tends to increase costs associated with sludge disposal; limitation of metals removal due to solubility constraints and interferences associated with complexing agents when stabilizing metal hydroxide sludge (Chhatwal 1997). Hydroxide precipitation depends on the insoluble metal hydroxide formation and this is hindered by complexation governed by the stability factors.

Siddiqui et al (1998) recovered chromium from spent chrome tanning liquor by precipitating in trivalent form using magnesium oxide and sodium hydroxide. The effect of temperature, alkali dose and initial chromium concentration on the removal efficiency was studied.

Neutralization of industrial effluent with lime could not bring the chromium level in the treated solution below 0.5 mg/L even in the pH range 10-11 as against the permissible limit of 0.1 mg/L prescribed by pollution control boards (Dikshit et al 1989). Chromium can form strong soluble complexes with several inorganics and organics resulting in an increase of soluble chromium even at high pH (Karra et al 1983).
An electroplating effluent containing hexavalent chromium on treatment with Ca(HSO₃)₂ followed by neutralization with Ca(OH)₂ at pH 8 resulted not even traces of hexavalent chromium in the wastewater (Ishiguro et al 1988). Reduction of hexavalent chromium using Fe filing as reducing agent in presence of coke dust as catalyst at pH 2-6, followed by pH adjustment to 8-9 resulted more than 90% metal removal (Wu 1989).

Ebata et al (1996) have studied the removal of heavy metals by treating with alkali metal silicates to precipitate as hydroxide and conditioning with the addition of coagulants to separate the sludge. The method removed heavy metals efficiently at low cost.

Peter et al (1989) studied the removal of heavy metals and oil from industrial wastewaters using hydroxide precipitation coupled with air flotation using sodium lauryl sulphate. This resulted in low concentrations of metals in the treated effluent.

The studies of Eckert and Edward (1994) showed that the wastewater containing heavy metals when contacted with carbon dioxide to lower the pH and treated with Fe²⁺ to co-precipitate metals as hydroxide followed by separation of metal hydroxide sludge provided substantially neutral wastewater with decreased content of heavy metals.

Arumugam (1976) studied hydroxide precipitation for the recovery of chromium from spent tan liquor. The optimum pH for maximum removal with lime was 6.6. Recovery of chromium hydroxide was done by settling, filtering and redissolving in sulfuric acid to form chromium sulphate which was recycled for further tanning. The use of lime was more economical than the use
of other alkalies. This precipitation process was the cheapest for the removal and recovery of chromium.

Sheffield (1981) investigated lime precipitation for removal of chromium, copper, iron, lead and nickel. These metals from the electroplating shops could be successfully removed by precipitation using hydroxide in conjunction with sulphate for enhancing the removal of chromium complexes.

Schilling and Fischevalsar (1989) studied the removal of Cu, Ni and Zn when present along with complexing agents using lime and chalk. This has led to less alkalinization of wastewaters than with lime alone. The residual concentrations of metal ions at different levels of complexing agents indicated the attainable level of <1mg/L for copper even in the presence of tartrate at pH 7-8.

Barrado et al (1998) treated the metal containing wastewater based on precipitation of metals in alkaline solution as metal-bearing ferrites of high magnetic permeability, which could be used in a variety of applications based on their magnetic properties. Under the optimum conditions and for concentrations of metal-binding organic ligands below $10^{-3}$ M, a removal efficiency of 99.9% and a chemically stable (inert) ferrite sludge of relative magnetic permeability 83.6 was obtained.

Though hydroxidation is effective for cadmium removal, it is not effective when the wastewater contains complexing agents such as cyanide. Most effective cadmium precipitation occurs between pH 9.5 and 12.5 (Jenkins et al 1964 and Culp and Culp 1974). However, it is difficult to

The hydroxide precipitation loses its efficiency at extreme pH values (Hill 1939). Complexation of lead with ammonia would prevent effective hydroxide precipitation (Patterson 1977).

Ayoub et al (2001) used sea water liquid bittern, as an inexpensive source of magnesium, in hydroxide precipitation process on wastewater alkalized with lime or caustic soda. The lime – liquid bittern process resulted in high removal (>90%) of cadmium, chromium, lead, mercury and zinc, and reasonably good removal of 71, 82, and 75% of arsenic, copper and nickel respectively.

Archana and Shukla (1994) studied precipitation of chromium and nickel in tannery and electroplating effluent using lime and caustic soda. The effect of temperature on the metal removal showed enhanced efficiency at elevated temperatures.

2.4.1.2 Carbonate precipitation

Carbonate reagents, such as calcium carbonate, sodium carbonate or carbon dioxide have been used to precipitate heavy metals from aqueous metal-bearing waste streams. Solubility of most metal carbonates fall between hydroxide and sulphide solubility limits. Calcium carbonate (lime stone) has been used due to its wide spread availability and high reaction rate.
Some of the disadvantages encountered when employing carbonate precipitation systems include longer retention times, lower solubilities and difficulty in mixing (Chhatwal 1997). Limestone is limited in its ability to treat wastewaters outside the operational pH range of 5-7. Since carbonic acid is formed while using carbon dioxide, it involves costs associated with the ultimate neutralization required prior to final discharge. Interferences such as cyanide, high pH and low carbonate levels will diminish the effectiveness of carbonate precipitation (Chhatwal 1997).

A complete reduction of Cr$^{6+}$ to Cr$^{3+}$ in the presence of Cd, Cu, Ni and Zn was obtained in the treatment of electroplating wastewaters at FeSO$_4$ doses exceeding the stoichiometric amount. After the reduction step Cd, Cr, Cu, Ni and Zn were removed by alkalinization to pH 9.5-9.5 with Na$_2$CO$_3$ (Kauspediene and Laumanskas 1989).

Singh et al (1996) studied the removal of toxic metals from plating waste by using an economically viable material, usar soil, as precipitant for the removal of chromium, copper, lead, nickel and zinc. The result indicated that usar precipitation technique was effective in the simultaneous removal of these metals. As usar soil contains sodium carbonate in major proportion, heavy metals are removed as their carbonate.

2.4.1.3 Sulphide precipitation

Metals removal can be improved by precipitating as sulphides (Cherry 1982). This is an extremely effective process for the removal of heavy metals (Peters and Ku 1987). The most commonly used precipitating agents include sodium sulphide and ferrous sulphide.

Sulphide precipitation offers 3 major benefits. They are:

i) Low residual metal levels in the treated water

ii) Effective precipitation at relatively low pH and


Sulphide precipitation removes the dissolved metal contaminants to the lowest levels possible while using the least amount of treatment chemicals and generating the least amount of sludge (Jancuk and Fisher 1995 and Soman et al 1993). The major advantage of the sulphide precipitation process is that very high metal removal efficiencies can be achieved due to extremely low solubilities of most of the metal sulphides (Cherry 1982, Clifford and Sorg 1986, Feigenbaum 1977, Scott 1979, Carpenter et al 1989 and Ku and Peters 1988). The sulphide precipitation is a viable technology to remove complexed metals from wastewater (Jancuk and Fisher 1995 and Ramani 1992). Sulphide precipitation is used to achieve the superior metal removal required by the discharge limit (Cherry 1982). As sulphides are less soluble than hydroxides, this method yields more complete metal removal than hydroxide precipitation (Wentz 1995).
Soluble metals can be removed by precipitating them as sulphide by the addition of sodium sulphide to the solution. Sodium sulphide has advantages over ferrous sulphide due to its high solubility, producing relatively high concentrations of dissolved sulphide which results in a rapid precipitation of dissolved metals leading to the efficient removal of heavy metals (Cherry 1982, Clifford and Sorg 1986, Feigenbaum 1977, Scott 1979, Carpenter et al 1989 and Ku and Peters 1988). Heavy metal complexes are more readily removed with the addition of soluble sulphides (Chhatwal 1997).

Sulphide precipitation can achieve low metal levels in the presence of complexing and chelating agents by breaking the complexes. It is capable of precipitating metals complexed with most of the complexing agents (Cherry 1982). Sulphide precipitation of metals in wastewaters has been the subject of several studies (Bhattacharyya and Ku 1984, Schlauch and Epstein 1977 and Robinson 1978) because of these potential advantages.

Laperle (1976) studied the removal of heavy metals from photographic effluents by sodium sulphide precipitation. Sulphide precipitation exhibits a better particle size distribution and settling characteristics than the corresponding metal hydroxide precipitation of cadmium and zinc (Ku and Peters 1986). Cadmium was removed from a synthetic wastewater containing cadmium 10ppm and cyanide 5 ppm by the addition of 1.25 equivalents of sodium sulphide, 25 ppm of sodium oleate and 5 ppm of FC-80 (acrylamide-dimethyl methacrylate copolymer), a cationic surfactant (Nakahiro et al 1982). The addition of sodium sulphide decomposed the cyano complexes and formed metal sulphide which was removed by froth floatation for 5 minutes at pH 5.5. The cadmium recovered from the froth was 97.7%.
The ease of dewatering is one of the best features of the sulphide precipitation method. Comparison of treatment of copper, nickel and zinc containing electroplating wastewaters by hydroxide and sulphide precipitation techniques showed that the sulphide sludge of nickel and zinc dewatered faster than their corresponding hydroxide sludge (Croy and Knocke 1980).

Prior to precipitation the hexavalent chromium needs to be reduced using suitable reducing agents such as SO₂, Ca(HSO₃)₂, sodium bisulphite, sodium meta bisulphate, FeSO₄, FeCl₂ etc. Chemical reduction method using FeS as reducing agent for the treatment of electroplating wastewater at pH <3.5 gave nearly 100% Cr(VI) removal efficiency (He 1989). Higgins et al (1981) found that sodium sulphide alone was not effective as reducing agent for hexavalent chromium in the pH range of 7-10. Such reduction is known to take place at pH values less than 3. It was found that sodium sulphide, in combination with ferrous sulphate aided the reduction even at high pH.

Sulphide precipitation using sodium sulphide to remove lead was studied using synthetic samples with concentrations in the range expected with effluents of metal finishing or metal production. The influence of pH, sulphide dosage and interference by chelating agents were evaluated. The efficiency of lead removal was more than 99% (Kamaraj et al 1989).

Battacharyya et al (1979) have studied the sulphide precipitation of cadmium, copper, lead, zinc and oxyanions of arsenic and selenium using dilute synthetic mixture and an actual copper smelting plant wastewater. It was observed that for both the wastes the overall removal of arsenic and other heavy metals was the best at pH values greater than 8. This result indicates that the
removal of heavy metals may vary with the constituents of the wastewater and their concentration.

Bhattacharyya et al (1981) investigated the feasibility of a combination of hydroxide and sulphide precipitation processes involving sulphide addition followed by lime. The results showed that only 60% of the theoretical sulphide dosage was required to provide effective removal of heavy metals.

Lefers et al (1987) studied the removal of the heavy metals from wet lime stone-gypsum flue gas desulphurization plants using seawater as process water. The method involved co-precipitation of metal hydroxides and sulphides employing ferric chloride and sodium sulphide with a polyelectrolyte. Sulphide addition was needed to obtain low concentration of cadmium and mercury in the treated wastewater.

Arsenic levels of 0.05 mg/L were obtained in the effluent by precipitation of arsenic as its sulphide by the addition of sodium or hydrogen sulphide at pH 6-7 (Patterson 1977 and Curry 1972).

Soman et al (1993) carried out the study of alkaline reduction of hexavalent chromium using ferrous sulphate and sulphide precipitation using sodium sulphide. Optimum ratio of sodium sulphide to ferrous sulphate dosage was ratio 1:3 at pH 8.

A comparison (Chhatwal 1997) of heavy metal removal efficiencies using lime and insoluble sulphide precipitation showed that precipitation by sulphide exhibited higher removal efficiency than lime.
Sulphide precipitation was adopted by Roennefahrt (1988) to treat wastewater from lead and zinc ore treatment plants. Removal efficiency of 91-98% Pb from battery industry wastewater had been achieved by Gashi (1988) through sulphide precipitation along with FeCl₃ as a flocculating agent (Bauch 1990).

### 2.4.1.4 Complexed heavy metal removal

Organic acids or their salts are used in the electroplating process to control the amount of free metals available for reaction. They stabilize the solution and retard precipitation (Wood 1982). The common complexing agents found in electroplating wastewater are ammonia, tartrate and citrate (Chhatwal 1997).

The presence of complexing agents in wastewaters are of great concern primarily due to their interaction with heavy metals, holding them in solution (Leu and Chang 1999). These complexes in wastewaters play an important role in transporting the heavy metals and preventing their removal by conventional precipitation processes (Peters and Ku 1987, Mayenkar and Lagvankar 1983, Nilsson 1971 and Gandhirajan and Selvi 2000). The major effect resulting from complexation is a dramatic increase in the solubility of the heavy metal ions (Laitinen and Harris 1960).

Citric acid and its salts are often used to clean the surface of metals because they cause less damage to the substrate metals (Martin and Banks 1974, Bradley et al 1975 and Blume 1977). Citrates have been reported to assist in the plating of many metals as buffers and complexing agents. Citric acid has been used effectively in electroless nickel plating baths (Othmer 1981).
Complexed metal wastes are often a product of electroless plating, immersion plating, etching and printed circuit board manufacture. The metals in these waste streams are tied up or complexed by the complexing agents whose function is to prevent metals from falling out of solution. In order to remove the metals it is necessary to break the complexes. High pH precipitation is a type of chemical precipitation particularly applicable to complexed metal wastes. The process involves adding chemicals to the wastewater, which bring about a drastic increase in pH, breaking the complex and precipitating the metals (Cherry 1982).

Studies reported by Ringmann et al (1997) demonstrated the removal of heavy metals from complexed state by precipitation with acylthioureas. After the treatment with acylthioureas, a decrease in metal content was achieved.

The presence of complexing agents such as cyanide and ammonia is a significant problem in achieving low residual concentration of copper in wastewater. Larsen et al (1973) reported a scheme in which the acid mine wastewater was first neutralized to pH 5 to precipitate iron and aluminium and then in the second stage treated at pH 6.5 with barium sulphide for the removal of other heavy metals. This resulted in the reduction of copper levels from 50-115 mg/L to below 0.5 mg/L.

Leu and Chang (1999) studied the electrolyte foam separation process to treat metal chelate solutions at varying pH values and varying surfactant to metal (S/M) ratios. The ionic competition characteristics of the metal chelate systems and the partitioning of chelates during the electrolytic foam separation process were also investigated by the FT-NMR method. Results of the FT-NMR analysis showed that, in the Ni-citrate-NDDTC
sodium diethyl dithiocarbamate) system with an S/M ratio of 4, the Ni-NDDTC chelate formation efficiencies at pH 4, 7 and 10 were 87%, 100% and 93%, respectively. These results were consistent with efficiency of Ni removal for 90 minutes of floatation. The efficiency of Ni removal in the Ni-citrate-NDDTC system was maximum at pH 7 (95%).

Gandhirajan and Selvi (2000) have carried out the study on the de-chelation of copper complex in printed circuit board industry wastewater. The wastewater containing copper chelates were destabilized by the addition of acid/ferrous sulphate prior to precipitation of copper as hydroxide.

2.4.2 Ion Exchange

Ion exchange is a unit process by which ions of a given species are displaced from insoluble exchange materials by ions of different species in solution. Ion exchangers are usually of the down flow, packed bed, column type. Wastewater enters the top of the column under pressure, passes downwards through the resin bed and is removed at the bottom. The ion exchange system design is sensitive to the specific ions to be exchanged, the control of influent suspended solids, and the treatment of regeneration solutions. Moreover, clogging or fouling of the resins also occurs (Corbitt 1999). It has various disadvantages such as the potential for chromatographic eluent peaking, yield variable effluent quality; needs disposal of spent regeneration concentrate and cannot be used for effluents with high total dissolved solids content.
2.4.3 Reverse Osmosis

If the pressure is increased above the osmotic pressure on the solution side of the semi permeable membrane, pure solvent will pass from the solution side into the solvent side. This is the basis of reverse osmosis treatment of wastewater. This process has the benefit of removing metals, which are less selectively removed by other techniques. The operation of an RO membrane is significantly affected by fouling, scaling, pH-temperature-pressure related hydrolysis and chemical or biochemical deterioration of the membranes. The limitations of reverse osmosis are its high cost, low efficiency and general lack of operating experience in the treatment of wastewater.

2.4.4 Electrodialysis

Electrodialysis is the process in which ionic components of a solution are separated through the use of semipermeable ion selective membranes. Application of an electrical current to pass through the solution in turn causes the migration of ions towards the oppositely charged electrodes. Because of alternate spacing of cation and anion permeable membranes, cells of concentrated and dilute solutions are formed.

2.4.5 Adsorption

Demands for a better quality of treated effluent have led to an intensive use of adsorption as a polishing technology after biological wastewater treatment units and also as a complete treatment method by itself. Activated carbon in granular or powdered form is the most widely used adsorbent for this purpose. Its high cost and substantial loss (10-15%) during
regeneration and low metal uptake capacity, however, have led to the search for cheaper substitutes. Unconventional materials, such as tree barks, peanut skins, onion skins, paddy husk, starch and cellulose xanthates, chitin, chitosan, etc have also been used (Bankar and Dara 1983, Dani and Dara 1983, Ansari et al 2000a and Ansari et al 2000b). Many of these processes generate other forms of hazardous wastes which require highly regulated and costly disposal processes (Dharmadhikari et al 2001).

2.4.6 Biological Treatment

2.4.6.1 Absorption of heavy metals by aquatic plants

The ability to absorb and concentrate metals from solutions has been investigated for variety of species. The concept of using plants as biological agents to remove heavy metals has drawn adequate attention. Aquatic plants are particularly important organisms for heavy metals uptake studies.

Various major aquatic plants or organisms that have been tried for the heavy metals removal in wastewater are microscopic algae, water hyacinth and duckweed. The use of algae for heavy metals removal is still limited because of relatively high expenses for harvesting and drying of algae.

The use of water hyacinth for heavy metals removal is increasing. Water hyacinth removes significant quantities of trace metals. The problem with water hyacinth is that they are sensitive to low temperatures and cost of plant harvesting and processing into by products is high. The water losses due to evaporation in water hyacinth system are 3-5 times larger than in free surface ponds. In water hyacinth system mosquito problem is high as the large volume
of plant foliage above the water surface provides excellent condition for mosquito development. Duckweed plants are also tried for heavy metals removal from wastewater.

2.4.6.2 Absorption of heavy metals by terrestrial plants

The process of accumulation or absorption of metals from water and soil is popularly termed as Phytoremediation. It is a promising new method that uses green plants to degrade, assimilate, metabolize or detoxify metals and organic chemicals.

Roots of many hydroponically grown terrestrial plants such as Indian mustard (Brassica Juncea), sunflower (Helin thuanuous), geranium and trees such as poplar and willows remove toxic heavy metals effectively from aqueous solutions.

2.5 RECOVERY OF HEAVY METALS

With the high cost of raw materials and pending land disposal restrictions, reclamation of raw materials from waste streams is the preferred treatment option. Many studies have concluded that a large part of industrial operational costs can be subsidized by the sale of the recovered metals. The excess heavy metals remaining in the electroplating effluents can be recovered by various methods. The sunlight induced hydrogen peroxide oxidation is a simple and promising method for the oxidation of metal sulphide into sulphate.
2.5.1 Sunlight Induced Hydrogen Peroxide Oxidation of Sulphide

Hydrogen peroxide has gained popularity because it oxidizes compounds without producing toxic byproducts. Oxidations using hydrogen peroxide are highly economic. Furthermore, hydrogen peroxide is a safe, readily available and cheap reagent (Haywood and Cooper 1998) and it is an extremely advantageous source of oxygen (Jacobsen and Wu 1999, Battioni et al 1988 and Anelli et al 1989). When hydrogen peroxide is exposed to sunlight it absorbs ultraviolet (UV) light and leads to the production of \( \cdot{\text{OH}} \) radicals by photolysis (Greiner 1966). Ultraviolet light has been shown to induce the peroxide oxidation rather than acting directly on the compounds (Cooper et al 2002).

Hydrogen sulphide and other reduced sulfur compounds can pose problems in both industrial and municipal treatment plants. In municipal collection and treatment systems, hydrogen sulphide is produced via the reduction of sulphates by bacteria under anaerobic conditions. In the presence of aerobic bacteria, hydrogen sulphide forms sulfuric acid, which corrodes metals and concrete. Hydrogen peroxide oxidizes hydrogen sulphide to elemental sulfur or sulphate. The residual hydrogen peroxide decomposes into dissolved oxygen, helping maintain an aerobic environment and preventing the formation of sulphide. The dissolved oxygen is also beneficial to biological treatment processes.

Reduced sulfur compounds also plague refineries, chemical plants, tanneries, food processing operations, pulp and paper mills and many other industrial facilities. Scrubbers can recover marketable sulfur from gases containing hydrogen sulphide and sulfur dioxide, but liquid waste streams with
ower concentrations of reduced sulfur must be treated with other methods. Today, much of this liquid waste disappears untreated into deep injection wells. As Federal and State regulations tighten, this simple solution is less available and the need for an inexpensive, effective chemical treatment is increasing.

Pala (2001) worked on the removal of sulphide from textile wastewaters accomplished by chemical oxidation with sodium hypochlorite and hydrogen peroxide, and catalytic oxidation by air. The removal efficiencies were found to be about ninety percent.

2.6 QUALITY CONTROL

2.6.1 General

Quality control is a set of measures within a sample analysis methodology to assure that the process is under control. It is an essential part of the analytical work without which the results cannot be relied upon.

The quality control procedure includes method calibration, standardization of reagents, assessment of individual’s capacity to perform the analysis, performance of blind check samples, determination of the sensitivity of the test procedure (method detection limit), daily evaluation of bias, precision and accuracy, laboratory contamination and other analytical interferences (American Public Health Association 1998).

2.6.2 Precision and Accuracy

Precision is the reproducibility of the analytical measurements. It is assessed by analyzing the replicate sets of same samples and specified by the
standard deviation. Accuracy refers to the closeness to the true or actual value. The factors, which affect the accuracy include the instrument stability and reproducibility, purity of reagents, the magnitude of matrix effect and environmental conditions in the laboratory.

Nafde et al (1998) determined precision and accuracy of heavy metals in river water and sediment samples by atomic absorption spectrophotometer and the sample values were lying within the control limits.

Muley et al (1995) determined the estimates of precision and accuracy associated with APDC-hexane extraction procedure in monitoring cadmium, chromium, copper, lead, nickel and zinc at the μg/L levels in sea water samples.

Generation of quality data is possible by improving the precision and accuracy of the methods. Padmaja et al (1996) made precision studies based on ten determinations of mercury when presents as inorganic, phenyl or methyl mercury compounds. The good recovery of each species clearly demonstrated that the proposed method worked satisfactorily for the sequential determination of mercury species.

Prudente et al (1994) checked the accuracy of analysis using standard reference materials (pond sediment). The standard error of this method in triplicate analysis was less than 5% for each element.

Analytical parameters such as stability of the system on a daily basis with precision and accuracy, and limits of detection or determination are the most important criteria for the quality check of the methods.
Windom et al (1989) routinely analysed estuarine sediment with each batch to assess the daily performance. When the deviation was more than twice the standard deviation, then the analyses were repeated.

Quality control of a method actually begins with the sample collection and includes all processes that follow until the resulting data are reported. McQuaker et al (1979) used selected reference materials to check the effectiveness of the digestion procedures. Similarly, to test the reproducibility and extraction efficiency, 16 samples of the river sediment were analysed which demonstrated that the acid extraction technique was able to recover the metals within the certified limits (Sinex et al 1980).

2.6.3 Quality Control Charts

Evaluation of daily performance can be easily executed through quality control charts. Precision control charts can be developed by repeatedly collecting data under controlled conditions. Accuracy control charts can be developed in the same way as precision control charts using spiked samples (Nafde et al 1998). The X-control chart gives the precision of a method and the S-control chart gives the accuracy of a method (Rump and Krist 1992).