CHAPTER - III
LITERATURE REVIEW ON METALS
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In this chapter an attempt has been made to review the literature related to sources, effects and removal of metals from wastewater streams.

3.1 INTRODUCTION

Metals are ubiquitous to man’s environment. With the process of evolution man has developed immunity towards their natural concentration. But with rapid industrialization, the use of metals like Cd, Zn, Hg, Pb, Cu, Ni and Cr has increased many folds as a consequence of which they are now being found in the environment in objectionable concentration.

Therefore, it is necessary to clean the waste from these pollutants before being discharged. Owing to the harmful effects of heavy metals to human beings and to aquatic life, environmental authorities have set permissible limits for different kinds of waters. The heavy metal ions are stable and persistent environmental contaminants, since they cannot be degraded and destroyed. These metal ions can be harmful to aquatic life and water contaminated by toxic metal ions remains a serious public health problem for human health. Metals are among main environmental concerns because of their unique characteristics; unlike organic pollutants, they are non-biodegradable and hence are accumulated by living organisms. The problem is aggravated by their high dispersion; they are widely spread in aquatic systems from where they enter the food chain. (Prasanna Kumar et al: 2006).

3.2 SOURCES OF METALS

In aquatic systems, the trace metals may be present as both soluble and insoluble forms within the water column, sediments and biotic tissues. Enriched levels of trace metals may occur naturally because of the weathering of a geologic substrate or volcanic emissions, or from anthropogenic sources such as industrial effluent, or nonpoint sources
such as urban storm runoff and atmospheric washout of particulate or gaseous emissions. Mining, fossil fuel combustion, smelting, plating, and other historical anthropogenic activates have altered the biogeochemical cycling of trace metals and frequently enriched the levels of trace metals in the environment. The release from a hazardous waste site may represent a significant local source, but rarely the only source of exposure to local biota.

Over the past decade, the consumption of metals and chemicals in the process industries has increased dramatically. Industrial uses of metals such as metal plating, tanneries, industrial processes utilizing metal as catalysts, have generated large amount of aqueous effluents that contain high levels of heavy metals. These heavy metals include cadmium, chromium, cobalt, copper, iron, manganese, mercury, molybdenum, nickel, silver, and zinc.

Chromium is the 6th most abundant element in the earth’s crust. Chromium compounds are among the most dangerous inorganic water pollutants (Natale et al: 2007). They are constantly released into the aquatic environment by natural processes (mainly by volcanic activity and weathering of rocks) and by anthropic sources, which in the last twenty years have become of leading importance in the worldwide emission balance of these substances.

Chromium, as environmental contaminant, can enter into the ecosystem from electroplating, metal finishing, chromate preparation, leather tanning, cooling towers of heavy industry, atomic power plants, mining, metallurgy operations etc (Manjeet Bansal et al: 2008). Chromium exists in nature mainly in two oxidation states, +3 and +6. It is bio-element in +3 oxidation state but mutagenic in +6 oxidation state. The hydrolysis behavior of Cr(III) is complicated and it produces mononuclear species Cr((OH)^2+\cdot, Cr(OH)^4-, neutral species Cr(OH)_3, and polynuclear species Cr_2(OH)_3 and Cr_3(OH)_4. Chromium sulphate [Cr(III)] is used as tanning agent, resulting in severe groundwater contamination around tanneries, which is transformed into chromium(VI).

Zinc finds wide applications in various industrial processes. Due to its remarkable resistance to atmospheric corrosion, zinc is commonly used to protect iron
from rusting, in the process called galvanization (Ajay Kumar Meena et al: 2005). Zinc is also used for the manufacturing of zinc white, brass, German silver, delta metal, Lithographic plates for the preparation of gold and silver by the cyanide method, in desilverization of lead by Parks process and as an anode material galvanic cells. Thus Zn(II) ions gain access to the river water environment from mining operations, wastewaters of electroplating, corrosion of galvanized piping, and dezincification of brass, besides other industrial wastes.

Potential sources of nickel bearing waste include ceramics, nuclear power plants, cryogenic containers, pollution abatement equipment (Shanmugavalli et al: 2006). Nickel will be present in the effluents of plating industries to the tune of 20 to 200 ppm.

Industries like rayan, printed board, metallurgical, copper smelters, metal processing and finishing, non-ferrous and electroplating industries are the major sources that discharge copper (II) ions into the environment (Kannan and Menaka Devi: 2005). Copper is discharged in various forms of complexes, such as copper-EDTA, cuprammine, copper fluoborate and copper complexes containing carboxylic acids, such as citric acid and gluconic acid.

Thus it is mainly the human activity, which has added enormous quantities of these elements in various components of the environment and for more clarity sources are summarized as follows.

3.2.1 Combustion of Fossil Fuels

An important source of heavy metals and trace elements in the environment is combustion of fossil fuels and organic matter. In coal, petroleum crude and dead organic matter most of elements occur in small amounts. Ash or fly-ash or unburned scum left after combustion is rich in number of toxic trace elements which are usually added to environment.
3.2.2 Contribution from Industrial Activity

A number of toxic trace elements are introduced into the environment as a consequence of industrial activity. Many industrial establishments burn huge amounts of fossil fuels for energy and extensively use a number of compounds of toxic trace elements. For example mercury finds widespread application in manufacture of plastics, chloralkali units, electrical and electronic industries etc.

3.2.3 Mining and Processing wastes

Mining of minerals and their processing to obtain the required metal have created enormous ecological disaster areas at many places around globe. Most of the mineral deposits occur as complex mixture of a number of elements. In the process of mining and extraction of particular metal the entire mass is excavated, laid bare and exposed to environmental agencies of weathering, degradation and transportation. The results in extensive contamination of surrounding areas. Smelting and subsequent treatment of ores results in emission of arsenic, lead, cadmium, mercury, sulphur dioxide etc. in large quantities.

3.2.4 Natural Sources

These include volcanoes, forest fires and sea salt sprays. There are significant, but it is the human activates that are increasing the environmental load of metals.

3.2.5 Other Sources

Municipal and industrial wastewater treatment plants are point sources of metal pollutants to water.

Paved roads and construction sites are among sources from which metal particulates can be blown away in wind or runoff with rainwater.

Fertilizers, pesticides, sewage sludge and animal wastes applied to soil have higher metal concentrations than natural soil levels.
3.3 EFFECTS OF METALS ON HEALTH AND ENVIRONMENT

Many trace metals are identical micronutrients for the maintenance of aquatic life, and toxic only when available to organisms at levels that exceed nutritional requirements. Trace metals such as copper, iron, zinc, manganese, cobalt, and selenium are essential to metabolism; yet, exposure of aquatic organisms to these same elements at elevated levels can adversely affect development and health, or cause death. Other trace metals such as lead, cadmium, and mercury do not play an essential role in daily maintenance, but adversely affect an organism if available at toxic levels.

The human body cannot process and dispose of the metals, therefore the metals will deposit in various internal organs. Large deposits may cause adverse reactions and serious damage in the body. Excess of heavy metals can lead to disease, such as Wilson’s disease, Argyria, cancer, heart and liver diseases, nervous system disorders and hypertension. Heavy metals from compounds in the body that can be carcinogenic and mutagenic even at very low levels. Therefore, not only the first generations are effected by heavy metals, but also the effects can be passed onto second and third generations in the from genetic abnormalities and birth defects.

Trace metal toxicity occurs when a receptor is exposed to available form of a trace metal for a sufficient duration at a concentration that elicits an adverse response. The potential for trace metal toxicity to aquatic organisms depends on numerous factors, including the chemical and physical characteristics of the water and sediment, composition and health of the biological communities present, and the magnitude and availability of the trace metal.

Upon exposure, uptake occurs by three main processes: from the water column through respiratory surfaces (e.g., gill); adsorption from water onto body surfaces; and from ingested food, particles, or water through the digestive system.

Chromium appears to be necessary for glucose and lipid metabolism and for utilization of amino acids in several systems. It is also responsible for the prevention of mild diabetes and atheroclerosis in human beings.
Chromium has been considered as one of the top 16th toxic pollutants and because of its carcinogenic and teratogenic characteristics on the public, it has become a serious health concern.

Hexavalent form is more toxic than trivalent and requires more concern. Strong exposure of Chromium (VI) causes cancer in the digestive tract and lungs and may cause epigastria, nausea, vomiting, severe diarrhea and hemorrhage. It is therefore, essential to remove chromium (VI) from wastewater before disposal.

Hexavalent Chromium at 10 mg/kg of body weight will result in liver necrosis, nephritis, and ultimately death in human beings; lower doses will cause irritation of the gastrointestinal mucosa. Hexavalent chromium in high doses may be the cause of digestive tract cancers in man. It can produce cutaneous and nasal mucous membrane ulcers and chromititis (from skin contact).

Among several heavy metals reported nickel possesses special characteristics. Nickel salts in water produce hazardous effects and nickel is carcinogenic. Nickel appears to be relatively non-toxic to mammals and exhibits only low toxicity but causes reduction in fecundity and survival by 50% at 1.6ppm. The plants and animals readily take up nickel in the ionic form (Ni^{2+}) from the soil or solution. Plant leaves are the major sinks for nickel. It is accumulated even in seeds and husk. Even low concentration of nickel is toxic to a wide variety of plants. Thus the movement of nickel in the ecosystem is great concern to mankind.

Zinc generated from phosphate fertilizers, distillery, pharmaceuticals and electroplating cause depression cough, vomiting, headache and metal fume fever.

These heavy metals can be extremely toxic as they damage nerves, liver, kidney and bones and also block functional groups of vital enzymes and they being non-biodegradable remain persistent. It is well perceived that there is a permissible limit of each metal, above which they are generally toxic and some are even hazardous. The toxicity due to metal ion is owing to their ability to bind with protein molecules and prevent replication of DNA and subsequent cell division.
3.4 DISPOSAL STANDARDS

The Indian standards for safe disposal of industrial effluents (metals studied) into receiving water bodies are shown in Table 3.1.

Table 3.1 Indian Standards for Disposal of Industrial Effluents

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Metal</th>
<th>Limits for discharge with inland surface water</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hexavalent chromium (as Cr+6), mg/l</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>Nickel (as Ni), mg/l</td>
<td>3.0</td>
</tr>
<tr>
<td>3</td>
<td>Copper (as Cu), mg/l</td>
<td>3.0</td>
</tr>
<tr>
<td>4</td>
<td>Zinc (as Zn), mg/l</td>
<td>5.0</td>
</tr>
</tbody>
</table>

3.5 HEAVY METALS REMOVAL TECHNIQUES

The commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, electrodialysis ion-exchange, reverse osmosis solvent extraction and ultrafiltration (Chandana Lakshmi et al; 2007).

3.5.1 Chemical precipitation

Precipitation of metals is achieved by the addition of coagulants, such as alum, lime, iron, salts and other organic polymers. The large amount of sludge containing toxic compounds produced during the process is the main disadvantage.

3.5.2 Electrodialysis

In this process, the ionic components (heavy metals) are separated through the use of semi permeable, ion selective membranes. Application of an electrical potential between the two electrodes causes migration of cations and anions towards respective electrodes. Because of the alternate spacing of cation and anion permeable membranes,
cells of concentrated and dilute salts are formed. The disadvantage is the formation of metal hydroxides, which clog the membrane.

3.5.3 Ion exchange

In this process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the ion exchange resin. The disadvantages include high cost and partial removal of certain ions.

3.5.4 Reverse Osmosis

It is a process in which heavy metals are separated by a semi permeable membrane at a pressure greater than osmotic pressure caused by the dissolved solids in wastewater. The disadvantage of the method is that is expensive.

3.5.5 Ultrafiltration

They are pressure driven membrane operations that use porous membranes for the removal of heavy metals. The main disadvantage of this process is the generation of sludge, selection of proper membrane.

Hence, the disadvantage, like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal has made it imperative to look for a cost-effective treatment method, that is capable for removing heavy metals from aqueous effluents. As alternatives, slowly, biological tools are being substituted in pollution abatement programmes. This technology has been loosely grouped together under the term ‘bioremediation.’ Biological methods, such as biosorption, bioaccumulation, phytoremediation for the removal of heavy metals ions may provide an attractive alternative to physico-chemical methods. Phytoremediation is the use of certain plants to clean up soil, sediment, and water contaminated with metals. The disadvantage include that it takes a long time for removal of metals and the regeneration of the plant for further biosorption is difficult.
3.5.6 Biosorption

Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake (Chandana Lakshmi et al; 2007). Biosorption is a species specific and metal specific phenomenon and that adsorption to a particular metal is a characteristic of an individual organism. Microorganisms uptake metal either actively, that is bioaccumulation and / or passively, that is biosorption. Feasibility studies for large-scale applications demonstrated that, biosorptive processes are more applicable than the bioaccumulative processes, because living systems (active uptake) often require the addition of nutrients and hence increases biological oxygen demand or chemical oxygen demand in the effluent. In addition, maintenance of healthy microbial population is difficult due to metal toxicity and other unsuitable environment factors. Potential for desorptive metal recovery is also restricted since metal may be intracellularly bound, metabolic products may complexes with metal to retain them in solution and mathematical modeling of a non-defined system is difficult.

3.5.7 Adsorption

Adsorption is highly effective, inexpensive and easy to operate among the physicochemical treatment processes. Consequently numerous low cost alternative have been studied.

3.6 SPECIFIC REVIEWS

Based on batch reactor experiments, the maximum percentage of nickel²⁺ removal of 92 % with a optimum contact time of 20 minutes by low cost sludge based activated carbon (SAC) has been reported by Raju and Saseetharan (2008). From the studies it is noted that, removal efficiently is directly proportional to pH is 4.3. It is also noted that granular form of SAC is more efficient when compared to the costlier conventional commercial activated carbon.

Rout et. al (2008) have examined adsorption behaviour of waste materials namely iron are slime. Red bauxite and low grade manganese are for Cu⁺². They have
studied effects of various experimental parameters, such as contact time, pH, temperature, adsorbent and adsorbate concentrations. They have recorded adsorption efficiencies at a pH of 5.25 as IOS>LMO>RB with the values of loading capacities as 12.8, 7.58 and 9.36 mg/g respectively. Further the authors observed the increase in Cu\(^{2+}\) adsorption with the increase in temperature for all the three adsorbents.

It is reported that the biomass of blue green algae Azolla Filiculoids can be used as an efficient and economic biosorbent for the removal of Cu\(^{2+}\) ions from aqueous solutions (Nedumaran and Velan: 2008). The maximum biosorption capacity of 893 mg/g of Azolla filiculoids has been observed at an optimum pH of 4.5 with an algae dosage of 1g/l.

Coconut coir pith, an agricultural solid waste was used as biosorbent for the removal of chromium (VI) after modification with a cationic surfactant, hexadecyltrimethylammonium bromide by Namasivayam and Sureshkumar: (2008) Optimum pH for Chromium (VI) adsorption was found to be 2.0. Reduction of Chromium (VI) to Chromium (III) occurred to a slight extent during the removal. The adsorption capacity of the biosorbent was found to be 76.3 mg/g, which is higher or comparable to the adsorptions capacity of various adsorbents reported in literature.

The feasibility of using pre-consumer processing agricultural waste to remove Chromium (VI) from synthetic wastewater under different experimental conditions has been reported by Manjeet Bansal et al. (2008). For this rice husk, has been used after pre-treatments (boiling and formaldehyde treatment). Effect of various process parameters, namely, pH, adsorbent dose, initial chromium concentration and contact time has been studied in batch systems. The removal of chromium was dependent on the phusico-chemical characteristics of the adsorbent, adsorbent concentration and other studied process parameters. Maximum metal removal was observed at pH 2.0. The efficiencies of boiled and formaldehyde treated rice husk for Chromium (VI) removal were 71.0 % and 76.5 % respectively for dilute solutions at 20 g/l adsorbent dose. The results revealed that the Hexavalent chromium is considerably adsorbed on rice husk and
it could be an economical method for the removal of hexavalent chromium from aqueous systems.

Removal of chromium (VI) from aqueous solution by walnut hull (a local low cost adsorbent) was studied by Xue Song Wang et al. (2008). The extent of adsorption was investigated as a function of solution pH, contact time, adsorbent and adsorbate concentration, reaction temperature and supporting electrolyte (sodium chloride). The chromium (VI) removal was pH-dependent, reaching a maximum (97.3 %) at pH 1.0. The uptake of chromium (VI) per weight of adsorbent increased with increasing initial chromium (VI) concentration up to 240-480 mg/l and decreased sharply with increasing in adsorbent concentration raging from 1.0 to 5.0 g/l. Compared to the various other adsorbents reported in the literature, the Walnut hull shows very good promise for practical applicability.

Adsorption of chromium (VI) ions on wheat bran has been studied using batch adsorption techniques by Nameni et al. (2008). The results of this study showed that adsorption of chromium by Wheat bran reached equilibrium after 60 min and after that a little change of chromium removal efficiency was observed. Higher chromium adsorption was observed at lower pHs, and maximum chromium removal (87.8 %) obtained at pH of 2.0. The adsorption of chromium by wheat bran decreased at higher initial chromium concentration and lower adsorbent doses. The results indicated that, wheat bran can be employed as a low cost alternative to commercial adsorbents in the removal of chromium (VI) from water and wastewater.

The removal of chromium (VI) from aqueous solution by rice straw, a surplus agricultural byproduct was investigated by Hui Gao et al. (2008). Chromium (VI) removal rate increased with decreased chromium (VI) concentration and with increased temperature. Decreased in straw particle size led to an increase in chromium (VI) removal. The authors concluded that, rice straw may be a new kind of low cost material which could convert chromium (VI) to the less toxic and more stable chromium (III) and could be used economically in the field to treat chromium (VI)-contaminated wastewaters.
Adsorption of chromium (VI) from aqueous solutions by spent activated clay has been investigated by Chih-Huang Weng et al. (2008). Spent activated clay (SAC), a waste produced from an edible oil refinery company after pressure steam treatment was used as an adsorbent. The rate of removal was found to speed up with decreasing pH and increasing temperature. The maximum adsorption capacities for chromium (VI) ranged from 0.743 to 1.422 mg/g for temperature between 4 and 40°C under a condition of pH 2.0. The studies conducted show the process of chromium (VI) removal to be spontaneous at high temperature and endothermic in nature.

Rumi Chand et al. (2008) have carried out studies to evaluate grape waste as a biosorbent for removing chromium (VI) from aqueous solution. An adsorption gel was prepared from grape waste by cross linking with concentrated sulfuric acid. It was characterized and utilized for the removal of chromium (VI) from synthetic aqueous solution. Adsorption tests were conducted in batch mode to study the effects of pH contact time and adsorption isotherm of chromium (VI). Cross linked grape waste gel has been found to be selective to chromium (VI) ion and highly effective for its removal from synthetic aqueous solution. The adsorption of chromium (VI) on the gel was highly pH dependent and maximum adsorption occurred at pH 4.0. The adsorption capacity was found to increase with increasing solute concentration as described by the Langmuir adsorption model. The maximum adsorption capacity of chromium (VI) was 1.91 mol/Kg at pH 4.0. The chromium (VI) occurs by esterification reaction. Since most of the industrial wastewaters contaminated with chromium (VI) are highly acidic, cross-linked grape waste gel can be good candidate for wastewater treatment. Due to large generation of grape waste every year and the every simple production process of cross-linked grape waste gel, it seems to be a promising adsorbent.

The effect of different parameters such as contact time, sorbate concentration, pH of the medium and temperature on removal of chromium (VI) from aqueous solutions using agricultural waste maize bran were investigated by Hasan et al. (2008). Maximum uptake of chromium (VI) was 312.52 (mg/g) at pH 2.0, initial chromium (VI) concentration of 200 mg/l and temperature of 40°C. Effect of pH showed that maize bran
was not only removing chromium (VI) from aqueous solution but also reducing toxic chromium (VI) into less toxic chromium (III).

The adsorption of chromium (VI) from aqueous solutions on formaldehyde treated sawdust (SD) and sulphuric acid treated sawdust carbon (SDC) of Indian rosewood, a timber industry waste, was studied at varying chromium (VI) concentration, adsorbent dose, and pH and agitation time (Garg et al; 2004). Similar experiments were conducted with commercially available coconut based activated carbon to compare the results. The chromium (VI) adsorption efficiency on SDC was higher than SD. An initial pH of 3.0 was most favorable for chromium (VI) removal by both the adsorbents. Maximum chromium (VI) was sequestered from the solution within 60 min after the beginning for every experiment. Narsi Ram Bishnoi et al.(2004) carried out investigations to evaluate the possible use of activated rice husk and activated alumina as the adsorbents of chromium (VI) from synthetic solution and the effect of operating parameters. The activated rice husk carbon was prepared thermally in two sizes 0.3 and 1.0 mm. Based on the present investigation the authors concluded that the adsorption capacity of ARH is comparable with the commercially based AA. The smaller the particle size, greater is the adsorption capacity, as evident from 93.28 % and 81.78 % Chromium (VI) removal with 0.3 and 1.0 mm ARH, respectively. The removal is pH dependent. The efficiency of ARH was fairly high at pH 2.0 whereas with AA it was at pH 4. Adsorption increased with increasing dose and time at initial stages and then it become somewhat constant. The adsorption efficiency for different adsorbent was AA > ARH (0.3 mm) > AARH (1.0 mm).

Renugadevi, et. al (2008) have carried out studies to evaluate the removal of chromium (VI) from aqueous solution using activated carbon from thiruvottukai (Crescantia cujeta L). Various parameters such as initial concentration of the adsorbate, contact time, pH and adsorbent dosage were studied by conducting batch mode experiments. Maximum removal of chromium (VI) was noted at pH 3.0. The equilibrium adsorption data correlated well with Langmuir and Freundlich adsorption isotherms. The adsorption of Chromium (VI) followed Lagergren first Order Kinetics.
Adsorption isotherms of chromium ions in aqueous solution have been experimentally measured on a granular activated carbon (GAC) and on a char of South African coal (CSAC) by Natale et al. (2007). Experimental results show that the adsorption capacity for the GAC strongly depends on solution pH and salinity, with maximum values around 7.0 mg/g at neutral pH and low salinity levels. On the contrary, the CSAC shows a smaller adsorption capacity near 0.3 mg/g, which slightly decreases by increasing pH and salinity levels. Chromium adsorption mainly depends on the availability of chromium ions in solution and on the occurrence of redox reactions between the surface groups and the chromium (VI) which lead to formation of chromium (III). The reduction of chromium (VI) and the following sorption of chromium (III) cations appear as the leading mechanism for chromium uptake on the CSAC. A similar behavior can be observed for the GAC at pH below 3.0

Arti Nigam and Rama (2003), carried out investigative studies on the removal of hexavalent chromium from aqueous solution using the sugar cane leaves as an adsorbent. The study involves batch experiments to find-out the effect of pH, concentration of Cr (VI), adsorbent dosage, contact time and temperature, since the removal of chromium was dependent on these factors. The removal of hexavalent chromium was found effective with 95% of removal at pH 2 to 3 and at 30°C temperature.

Gharde et al. (2005), conducted adsorption studies on the removal of chromium from aqueous solution using Fredonia of elefuntum fruit shell as an adsorbent. Studies indicated that sorption of chromium increased with the increase in pH and contact time. The removal efficiency was found good at 60 min. contact time; hence ferronia elefuntum fruit shell is economical and effective in removing heavy metals from industrial wastewater.

The ability to remove chromium (VI) from the contaminated water by transforming chromium (VI) to chromium (III) by Ipomea aquatic a wetland plant, which floats in water bodies has been studied by Subhas Chandra Bhat, et al. (2005). They found that contact time required to bring down chromium (VI) concentration below the permissible level (0.05 mg/l) is 30 to 40 days for this plant and that varies with varying
initial concentration. The lower level of contamination requires greater contact time than the higher one to bring down chromium (VI) below the permissible level.

Maize bran a low cost biosorbent has been used for the removal of Cu\(^{+2}\) from wastewater (Singh et al: 2004). The effect of various parameters, such as contact time, adsorbate concentration, pH of the medium and temperature have been studied. The conditions for the optimum of Cu\(^{+2}\) (90.0 %) were found at pH of 6.5, initial Cu\(^{+2}\) concentration, 40.0 mg/l and temperature 20\(^{\circ}\)C.

The adsorption studies on the removal of copper from aqueous solution using carbon aerogel as well as locally available weathered cost and sawdust (treated) was carried out under varying experimental conditions by Meena et al: (2004). The maximum adsorption was observed to be a function of the solution pH, contact time, initial concentration of copper ions and adsorbent dose. At contact time of 24 hours, adsorbent dosage of 1g/100ml, initial concentration of metal -4mg/l, 77.2 and 92 % removal by GAC and treated sawdust have been recorded.

Wheat bran a low cost biosorbent has been used for the removal of Cu\(^{+2}\) from wastewater by Singh et al: (2004). The effect of various parameters, such as contact time, adsorbate concentration, pH of the medium and temperature have been studied. The conditions for the optimum removal of Cu\(^{+2}\) were found as 94 % at pH of 8.0, initial concentration: 40 mg/l and temperature 20\(^{\circ}\)C. Thus the wheat bran has been found to be very effective biosorbent for the efficient removal of Cu\(^{+2}\) from wastewater.

Studies on adsorptive removal of copper and nickel ions from water using chitosan coated PVC beads were carried out by Srinivasa et al. (2009). The effect of pH, agitation time, concentration of adsorbent and amount of adsorbent and the extent of adsorption was investigated. The experimental data were fitted to Langmuir and Freundlich adsorption isotherms. The data were analyzed on the basis of Lagergren pseudo first order, pseudo-second order and Weber-Morris intraparticle diffusion models. The maximum monolayer adsorption capacity of chitosan coated PVC sorbent as obtained from Langmuir adsorption isotherm was found to be 87.9 mg/g for Cu\(^{+2}\) and 120.5 mg/g for Ni\(^{+2}\) ions respectively. In addition, breakthrough curves were obtained.
from column flow experiments. The experimental results demonstrated that chitosan coated PVC heads could be used for the removal of Cu\(^{+2}\) and Ni\(^{+2}\) ions from aqueous medium through adsorption.

The removal of Zn\(^{+2}\) ions from dilute aqueous solution using maize (zea mays) leaf as the adsorbent is reported by Adesola Babarinde et al. (2008). The batch biosorption studies have shown that the biosorption is pH dependent and the optimum pH for the removal is in the range of 4-7. The amount of zinc ions biosorbed increased with increased initial metal ion concentration. Maximum adsorption was obtained within the first 40 minutes on an average 90 – 92 % zinc removal was recorded. Thus the authors recommended the use of maize leaf biomass, an agricultural waste, as potential biosorbent for the removal of Zn\(^{+2}\) from aqueous solutions.

A simple and cost effective treatment procedure was proposed for the removal of heavy metals through the adsorption on sand. (Muhammad Masud Aslam et al.: 2004). This study records lab scale experiments to test efficiency of sand on removing a heavy metal, Zinc (II) from wastewater of electroplating industry. This method of heavy metals removal proved highly effective as removal efficiency increased with increasing pH ranging from 71-87 % and maximum adsorption occurred at depth 1 m as compared to 0.6 m and 0.8 m depth. Since sand is cheap and easily available, the authors concluded that the sand filtration, which is efficient and effective, has the potential to be used for removal of heavy metals from can successfully be used for removal of heavy metal from water and industrial wastewater.

The possibility of cadmium (Cd\(^{+2}\)) and zinc (Zn\(^{+2}\)) toxic cations removal from simulated liquid effluents by a relatively innovated treatment, named galvanochemical, using the galvanic pair iron-carbon, was investigated Prochaska et al. (2001). The study showed that there is a great potential for the application of galvanochemical method to the purification treatment of metal-laden wastewaters from small-to –medium industrial units, as the residual metal concentrations were found to be below the legislation limits, under the optimized operating conditions.
Scott et al. (2001) tested four filtration media in controlled laboratory experiments to determine their effectiveness for concurrent metals removal and toxicity abatement in synthetic stormwater. Media tested included commercially available leaf compost (CSF®) media, a zeolite/perlite mix, and a polyamine sponge, as well as the recently developed citric acid modified soybean hull media. The CSF® media removed up to 75% of the zinc and reduced toxicity significantly for influent concentrations of up to about 300 ppb zinc. Variations of the CSF® media improved zinc removal modestly compared to the standard version. The soybean hull material removed 80 to 99% of the zinc over all influent concentrations though it reduced pH to toxic levels. After pH adjustment, the effluent from the soybean material was non-toxic overall concentrations tested. Augmenting the soybean material with leaf compost media or activated carbon effectively buffered effluent pH to circum-neutral ranges. Other media tested removed modest amounts of zinc and were capable of sufficiently reducing toxicity only in the lowest concentrations tested, while some media appeared to generate toxicity.

Studies on the removal of zinc by adsorption on two types of flyashes, namely Bokaro Thermal Power Plant Fly ash and Fluidized Bed combustion fly ash from Tata steel, Jamadoba were carried out by Srivastava, et al. (2007). Batch adsorption experiments were done. The effects of various parameters such as contact time, initial concentration, pH, fly ash dosage on the removal of zinc ions were studied. In case of fluidized bed combustion fly ash the maximum removal capacity was 0.0515 mg of Zn\(^{+2}\) gm of ash, in thirty minute where as in case of Bokaro Thermal Power Plant flyash the maximum removal capacity was 0.0925 mg of Zn\(^{+2}\)/gm of ash. The loss on ignition of fluidized bed combustion fly ash was 17.15% and that of Bokaro thermal Power Plant fly ash was 6.67%. So the quantity of zinc by the two types of flyash may be related to the difference in their unburnt carbon. Higher the unburnt carbon better is the adsorption capacity. At low pH values the flyash particle is positively charged while at high pH value the flyash particle is negatively charged. So adsorption is favored when the particles are negatively charged, that is in alkaline medium.

The effectiveness of soluble starch Xanthate (SSX) for removal of Cd(II), Chromium(VI) and Cu(II), insoluble starch Xanthate (ISX) for Chromium (VI) and
Cu(II) have been evaluated under different aqueous phase conditions (Vinod Tare et al.: 1988). Comparison between ISX and SSX, based on the equivalents of metal removed per mole of ISX/SSX added indicated that ISX has better binding capacity for metals. However, with due consideration to yield and chemical requirements for the synthesis of ISX and SSX, SSX appears to have higher capacity for metal removal. The order of preference of metal binding capacity of SSX is found to be as Cr (VI) > Cu (II) > Cd (II) whereas of ISX as Cr (VI) > Cu (II).

Bilquees Ara Siddiqui, et al. (1999), Carried out series of experiments in batch process to determine the adsorption studies on phosphates treated sow-dust for removal of Cr (VI), Nickel and Zinc removal from aqueous solution of electroplating waste. The effect of initial concentration pH and adsorption doses were studied and they observed that the removal of these metals were dependent on the contact time, pH, Adsorbent dosage.

Nickel biosorption ability was evaluated in two bacterial strains: Acinetobacter baumannii UCR-2971 and Pseudomonas aeruginosa UCR-2957, resulting in greatest adsorption at pH 4.5 and a residence time of 100 minutes (Carlos et al.: 2006). The maximum adsorption rates were 8.8 and 5.7 mg/g for A. baumannii and P. aeruginosa, respectively; It is suggested that both strains could be used for wastewater treatment, as long as the concentration of Ni\(^{2+}\) is within the range of 4-13 mg/l.

Feasibility studies of using treated fly ash in the removal of nickel from aqueous solutions were performed by Suwan et.al. (2006). Batch adsorption experimentation were used to investigate the adsorption efficiency of treated fly ash for the removal of nickel. Concentrations of nickel varied in the range of 1-10 mg/l. The adsorption efficiency was found to increase with increasing tested fly ash concentration. At treated fly ash concentrations above 1.25 g/l the removal was almost instantaneous. Adsorption equilibration was usually attained within 30 min at a pH of 3-5. 86 to 92% removal of Ni\(^{2+}\) from industrial wastewaters was recorded.

Studies on the removal of metal ions, like nickel (II) by adsorption on surface of orange peel (OP) was carried out at room temperature (30±1°C) by Kannan and
Inbaraja (2006). The effect of process parameters like initial concentration, contact time, dose of adsorbent (op) and initial pH was studied for the removal of metal ions. The studies revived the 20 to 35 % removal of Ni$^{2+}$ at optimum pH, adsorbent dosage and contact time of 5.0, 110 gm/l and 50 minutes respectively.

Activated carbon prepared from silk cotton hull was used to remove Ni$^{2+}$ from aqueous solution by adsorption (Shanmugavalli, et al.: 2006). Batch mode adsorption experiments were carried out by varying contact time, metal-ion concentration and pH to assess kinetic and equilibrium parameters. The adsorption capacity of 56.40 mg/g of activated carbon at initial pH of 5.0 for the particle size 125 – 250 μm was observed

Adsorption characteristics of nickel on activated carbon at different pH values have been evaluated by Amal Raj (2004). The adsorption capacity of activated carbon was found to be dependent on pH of influent solution and better at pH below 4.5 the author reports 85 to 95 % removal at pH below 4.5.

Murali and Sai Suseela (2001), studied the removal of nickel from aqueous solution by using Tephrosia purpurea leaf powder as an adsorbent. The study was carried out in batch experiment in three phases to find-out the effect of concentration of nickel at different concentrations different contact time, rpm and dosage of adsorbent. Each phase was involved with different contact time, rpm and dosage and results of each phase were recorded. In the third phase at a contact time of 60 min. and at 40 rpm with a dosage of 4.5 gm the removal of nickel from aqueous solution was found effective with 97.86 % of removal and with same set at 1.5 gm of adsorbent the removal of nickel was found to be 58.65 %. They revealed that the percentage of removal increased with increased doses; hence the Tephrosia purpurea can be useful adsorbent for removal of nickel from industrial wastewater.

The biosorption of Zn$^{2+}$, Ni$^{2+}$ and CrO$_4$ was studied over a range of metal ion concentrations, adsorption time, pH and co-anions, by fungal mycelium pellets of Aspergillus niger 405 as an adsorbent (Zeljka et. al.: 2000). The results showed better biosorption for the ions at pH ranging from 4 to 6. On the contrary, pH values from 3 to 7 had no influence on sorption of chromium.
Studies were carried out for the removal of zinc metal from synthetic stock solution, by the adsorbent material bentonite. (Prasanna Kumar et al. 2006). Parameters studied include time of contact, size of bentonite particles, dosage of the adsorbent, initial concentration of the solution, initial pH of the solution and volume of the solution.

The sawdust used as adsorption was sieved (50 – 60 mesh) and washed several times with distilled water. It was than treated with 0.1M aqueous solution of Di –sodium hydrogen phosphate for 24 hrs. The material was then filtered and washed several times with distilled water to release phosphate and dried at 40°C in an oven. Than 50 ml of solution containing required amount of metal ions was treated with 1mt of this adsorbent in 250ml conical flask. The mixture was filtered after contact time of 24hrs and filtrate was analyzed for heavy metals in Atomic Absorption spectrophotometer.

They found that % adsorption of Zn (II), Ni (II) and Cr (VI) is maximum in neutral media. The % of adsorption remains 80 % even up to their initial concentration of 30 mg. maximum adsorption is observed at pH 7 – 8, the adsorption of these metals follow the trends at various pHs

\[
\begin{align*}
\text{pH7:} & \quad \text{Cu (II) > Zn (II) = Ni (II)> >Cr (VI)} \\
\text{pH2:} & \quad \text{Cr (II) > Cu (II) > Ni (II) > Zn (II)}
\end{align*}
\]

Akira OTSUKI et al. (2004). Reported that nickel and zinc found in wastewater from industrial factories can be effectively removed by physicochemical adsorption using mainly natural zeolite. They achieved best results while 50 mg/l of natural zeolite and 0.5 mg/l of aluminum ion were added into solution at pH 10. More then 98 % of nickel and zinc and more then 94 % of phosphorus were removed from the wastewater.

Anima et al, (2004) carried out studies to investigate the removal of nickle by rice husk in a batch process. They reported the increase in adsorption percentage with increase in contact time, adsorbent dosage and pH and decrease in adsorption with increase in concentration of the metal ion. 89 % of nickle removal from electroplating industrial effluent by rice husk has been reported by the authors.
Removal of hexavalent chromium from aqueous solutions has been investigated using the mixture of fly ash and commercial activated carbon. From the batch type experiments conducted with different concentration of chromium at different pH value. The authors concluded that the adsorbents can remove 90 - 100% of hexavalent chromium with intermittent hand shaking condition at pH - 2.0

97 % chromium (VI) removal by activated carbon (Prepared from simarouba glance seed shells) impregnated with zincchloride in 1:2 ratio at pH 3.0 has been reported by Neelavathi et. al, (2004). They have also observed much lower activities of adsorbent impregnated in ratios of 1:1 and 1:3.

88 % removal of total chromium and greater than 99 % removal of hexavalent chromium by activated carbon prepared from carbonization of rice husk with sulphuric acid followed by CO2 activation is observed by Srinivasn et. al (1988). Further based on column studies, the authors reported the capacity of 8.9 mg/g and 6.3mg/g for rice husk and commercial carbons respectively for Cr (VI) removal. Also they reported the average Cr (VI) recovery of 22.5 % and 30.6 %, when alkali followed by acid were used for regeneration of rice husk and commercial carbon respectively.

The batch studies conducted with varying experimental conditions like pH. Particle size concentration. Contact time and dosage revealed that the activated carbon derived from sorghum vulgare (dried stem of jowar) has good Cr (VI) removal potential (Shashikant and Rajamanya : 2003) the activated carbons prepared by physical and chemical activation using H$_2$ SO$_4$, H$_3$ PO$_4$ activating agents of different impregnation ratios under varied experimental conditions exhibited the chromium (VI) removal varying from 60 to 92 %. They have observed the increase in removal efficiency with decrease in pH, with maximum removal at pH 2.0.

Good sorption capacity of activated alumina for hexavalent chromium and no pronounced effect of pH on the sorption capacity has been reported by Sudipta Sarkar and Anirban Gupta (2003). Based on batch studies they have conducted to investigate the suitability of activated alumina for removal of hexavalent chromium from electroplating wastewater. Also based on the column studies carried out by using
synthetic chromium wastewater. They concluded that for practical application of chromium removal, reasonable depth of column may be very useful.

The batch mode experiments were conducted to access the Cr. (VI) removal efficiency from aqueous solution using carbon waste from domestic water purifier under varied experimental conditions like initial concentration of Cr (VI), pH, adsorbent dosage and agitation time, temperature being 30° C by Renuga devi et. al (2007). The observations of their studies are as listed below.

- An increased percentage removal from 67 to 75 % was observed with 100 mg of adsorbent in contact time of 180 min when the initial concentration of the Cr (VI) solution was varied from 1.2 to 0.6 mg/l.
- The removal increased from 66 to 74 % in 180 min of agitation time for the adsorbent dosage variation of 60 to 120 mg.
- The removal increased from 54 to 61 % in 60 min of agitation and 69 to 81 % in 180 min of agitation time when the pH varied from 6.3 to 3.5.
- The removal increased from 41 to 69 % when the agitation time was varied from 10 to 180 min at pH 6.3, when the initial concentration of Cr (VI) solution used was 1 mg/l and the adsorbent dosage was 100 mg.
- The adsorption follows lagergren first order kinetics.

The studies carried out by Shantha Veerana Goud et. al (1997) to evaluate the potential of water hyacinth in removal of chromium from chrome tannery effluent revealed that the plant is capable of removing 75% of the chromium when the chromium concentration in the wastewater is 25 mg/l. They carried out studies considering the variables like pH, stirring effect and the initial chromium concentration of the tannery effluent. They have noticed the inverse relation between initial concentration and percentage removal and the better performance at neutral pH.

Removal of chromium (VI) using iron and aluminum electrodes by electro coagulation has been reported by Mahesh et. al (2007). The method was found to be highly efficient and relatively fast compared to chemical coagulation and adsorption by activated carbon. Results obtained with synthetic wastewater revealed that most effective
removal capacities of hexavalent chromium in a range of admissible legal levels could be achieved with a pH range of 7 and 8 and current density in the range of 6.7 to 26.7 ma/cm².

40 to 99 % removal of chromium from spiked solutions during the seven day exposure by common aquatic ferns namely Salvinia Molesta Mitchell and Azolla rubra R. Br has been reported by Shiny et. al, (2004). Treatability studies with 8 mg/l of initial metal concentration showed 70.6 and 50 % of removal by Salvinia and Azolla respectively. On the other hand it was found that both Salvinia and Azolla could remove up to 99 % chromium at a concentration of 2 mg/l.

Aspergillums Niger biomass was proved to be an ecofriendly, low cost alternative for the removal of chromium (VI) from industrial wastewaters (Sneha and Varsha : 2008). The authors observed that the process was pH dependent, favouring maximum sorption of 20.17 % at pH 2.0.

Increase in Cr (VI) adsorption with increase in initial concentration of Cr (VI) and adsorbent dosage (Bentonite clay) and with decrease in pH has been reported by Neetu Tewari et al (2005). The adsorption capacity of Cr (VI) by bentonite clay was found to decreased from 1.3 mg/g to 0.3 mg/g with increase in pH from 2.0 to 6.0. Increase of adsorbent dosage from 2.0 to 10.0 mg/l has resulted in increase of Cr (VI) from 7.8 to 28.0 mg/l.

82 % (pH: 3) and 84 % (pH: 4) removal of copper and zinc respectively at contact time of 3 hrs from electroplating industrial waste water biomass has been reported by Kanimozhi and marline sheela (2008). The authors stated that as compared to the commercial activated carbon the removal efficiency of the biomass studied is approximately same but as compared to the cost, it is cheap.

The results obtained from the bacterial studies (Khasim Beebi et.al: 2007) showed that the live bacterial biomass of gram positive Bacilli, Diplo cocci and pseudomonas species has the potential to remove 94 % nickel from single metal solution.
99.6% removal of nickel ions from industrial plating effluents by gibbsite form of activated alumina at an optimum contact time of 60 minutes has been reported by Revathi et al (2005). They have observed the increase in percentage removal of nickel with increasing amount of alumina. They have also reported that the gibbsite form of alumina is more efficient in removing nickel ions compared to commercially available alumina.

Srivastava et al (2007) have carried out batch adsorption experiments to access the removal of zinc by adsorption on two types of fly ashes namely Bokaro Thermal Power plant fly ash and fluidized bed combustion fly ash and fluidized bed combustion fly ash from Tata steel and reported the adsorption of 0.0925 mg and 0.515 mg of Zinc Per gm of ash respectively. They concluded that the percentage removal is related to percentage of unburnt carbon present in fly ashes and zinc removal is more effective in alkaline medium.

The effectiveness of fly ash generated during burning of coal in boilers, in adsorbing soluble copper present in the effluent of printed circuit board manufacturing plant was studied in batch mode (Kapadia et al : 2000). The pH of effluent around 6.0 and contact period of 1 hr gave optimum removal of copper. The amount of copper adsorbed increased with increasing concentration of copper in wastewater. The removal was 62% at 60 mg/l initial copper concentration and increased up to 98% with decrease in concentration up to 2 mg/l at 5% dose of flyash.

Maximum removal of 95% of hexavalent chromium at pH 2.0 by rice straw from aqueous solution has been reported by Samanta et al (2000) based on the studies carried out by them to evaluate the chromium removal capacity of rice straw in an agitated a packed bed column under varying process design parameters namely temperature. Concentration, adsorbent dose and pH of the solution.

A carbonaceous sorbent prepared from an indigenous plant namely pitchellobium dulce benth by acid treatment and also by pyrolysis and was tested for its efficiency in removing Cr (VI) by Prabhavathi Nagarajan et al (2006). The process parameters studied include agitation time, concentration, carbon dose, pH and temperature. PPC
adsorption capacity of 45.63 mg/g and 16 mg/g for APC were observed. Thus the authors opined that PPC carbon is a better adsorbent than APC for Cr (VI).

**Goyal and Surendra kumar (2005)** have recorded the maximum Cr (VI) reduction of 85 to 92 % at optimum pH by magnesium sulphite in the aqueous phase and subsequent precipitation. No influence of temperature on Cr (VI) reduction was observed by the authors.

From the studies on removal of Cr (VI) from aqueous solution using activated soyabean hull carbon, by **Jambulingam et al (2005)** reported that soyabean hull is an effective low cost adsorbent and the adsorption of Cr (VI) ion is dependent on the initial concentration of the metal ion, pH, amount of adsorbent and agitation time. They have recorded maximum removal at pH 2.0.

Removal efficiency of 40 to 76 %, 27 to 75 % and 39 to 91 % of chromium (VI) from aqueous solutions by carbonized organic materials namely papal bark, rice husk and saw dust respectively has been reported by **Joshi and Srivastava (2005)**.

Electrolytic separation of chromium (VI) from Chrome Tannery waste water using a stainless steel plate as cathode and a graphite rod as anode was studied by **Verma Babita and Shukla (1999)**. Almost 100% Chromium reduction was observed at 500 mg/l concentration with electric potential maintained at IV.

98 % and 94 % and 92 % and 96 % adsorptive removal of Ni (11) and Zinc (11) respectively by treated GAC and carbon aerogel respectively under optimized conditions of pH-8 and dosage of 1.2 g/100ml, for 3 mg/l Ni (11) and Zine (11) from aqueous solutions in 48 hr contact time has been reported by **Ajay Kumar Meena et al (2005)**. They found that adsorption is pH dependent and maximum adsorption occurs at pH 8 and 6 for treated GAC and carbon aerogel respectively.

The maximum adsorption of 88.66 and 44.94 mg/l of Cr $^{+6}$ and Cu$^{+2}$ respectively at the initial concentrations of 193.66 mg Cr$^{+6}$/l and 105 mg Cu$^{+2}$/l at optimum pH of 2.0 and 3.5 respectively by microorganisms namely. Staphylococcus saprophyticus were reported from industrial wastewaters by **Semra Ilhan et.al (2004)**.
Removal of heavy metals namely zinc and copper from industrial wastewater effluent under varied experimental conditions using hydrogen peroxide was investigated by Badmus et al (2007). Maximum reduction of 85.5 and 82.23 % of zinc and copper respectively at optimum pH of 7.6 temperature 30°C, 1.5 % hydrogen peroxide concentration and 60 min holding time were recorded by authors.