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*Review of Literature*

## **2.0 REVIEW OF LITERATURE**

The review of literature pertaining to the study “Adsorption of nickel(II) and chromium(VI) from synthetic metal solutions using powdered human hair as adsorbent” is discussed under the following headings:

### **2.1 ENVIRONMENTAL POLLUTION**

### **2.2 INDUSTRIAL POLLUTION**

### **2.3 METAL POLLUTION**

#### **2.3.1 Chemistry of heavy metal pollution**

#### **2.3.2 Bio-importance of heavy metals**

#### **2.3.3 Heavy metal poisoning and biotoxicity**

#### **2.3.4 Biochemistry of toxicity**

### **2.4 INDUSTRIAL WASTE WATER TREATMENT**

#### **2.4.1 Metal removal by adsorption**

#### **2.4.2 Bioremediation**

#### **2.4.3 Biosorption**

### **2.5 METAL SORPTION**

### **2.6 HUMAN HAIR AS AN ADSORBENT**

### **2.7 ADSORPTION ISOTHERM**

### **2.1 ENVIRONMENTAL POLLUTION**

Environment literally means the surrounding. It can comprehensively be defined as the sum total of all the conditions and influences that affect the development and life of organisms. Pollution has been recognized as any undesirable change in the physical, chemical and biological characteristics of our air, land and water, which may harmfully affect the human, animal and plant life. Thus, the contamination of environment with impurities which make it unfit for its intended use is known as environmental pollution and any substance whose presence in the environment causes pollution may be termed as pollutant (Omkar, 2003).

Environmental contamination is the release of the substances into the environment at measurable concentrations, while pollution implies the manifestations of measurable effects produced by substances on the living systems (Kudesia, 2000).

The best definition of environmental pollution refers to the contamination of earth's environment with materials that interfere with the human health, the quality of life or the natural functioning of ecosystems (living organisms and their physical surroundings). Although some environmental pollution is a result of natural causes such as a volcanic eruption, most is caused by human activities (Chatwal and Sharma, 2005).

Environmental pollution is the unfavourable alteration of our surrounding (Kudesia, 2000). These alterations may affect man directly or indirectly. Environmental pollution causes (1) health problems – by affecting human health and lives, (2) economic problems – by affecting human property and materials, (3) ecological problems – by disturbing a balanced ecosystem, interfering with the conservation of natural resources and threatening the mere existence of some species and (4) aesthetic problems – by generally affecting human senses (Kanan, 1991).

## **2.2 INDUSTRIAL POLLUTION**

Environmental pollution is becoming the global problem which is an important issue as water is used directly for various purposes. The major sources of water pollution are industrial effluents and the wastewater generated from various industries, discharged to the common drainage. The effluents pollute not only the nearby water resources but also contaminate the nearby soil and pass to other drinking water resources and hence may cause pollution of drinking water (Lokhande and Vaidya, 2004).

Industrial pollution includes air, water and chemical pollution caused by industries. Industrial pollution began when our country went through the industrial revolution. Mostly all parts of the world are affected in some way by industrial pollution. The smog, smell, and contamination of food or water are some direct effects. Remote areas of the world are affected indirectly by industrial pollution.

The rapid growth of human population, over exploitation of natural resources, the developments in the sector of agriculture, industry, public health and the increase in the means of transport have contributed extensively to the presence of various metals in the environment (Ebenezer, 2003).

An industrial technology improves the characteristics of industrial discharge sources which becomes complicated and the toxicity of industrial waste water can also become more complicated and heavier. They can influence the operational efficiency of the existing waste water facilities and cause them not to meet the more stringent effluent standards (Sponza, 2002).

Industrialization has its inevitable effect on pollution of air, water and soil based on the type of industry, nature of raw materials used and the manufacturing processes involved (Dolar *et al.*, 1972; Abdul-Baki and Anderson, 1973; Bose *et al.*, 1973; Ghosh, 1966). Industrial effluents are being used for irrigation in dry areas. These effluents do not contain nutrients that enhance the growth of crop plants but also have other toxic materials (Somashekar *et al.*, 1984).

About 80-85% of water consumed by the industry is discharged as waste water containing organic and inorganic pollutants and colouring materials. The nature and volume of the effluent discharged varies from industry to industry and depends on the production capacity, raw material used, types of product manufactured, processes involved and recovery of chemicals (Jain *et al.*, 2008).

The untreated effluents by industrial facilities are primarily responsible for the water pollution problems. It is estimated that more than  $2.6 \times 10^{11}$  kg of hazardous chemical wastes are being generated annually by the manufacturing units in U.S.A. alone, and that only 10% of these wastes are disposed in an environmentally safe manner. Each manufacturing unit uses a specific chemical in its processes and hence the resulting untreated wastes have the same type of contaminant in them (Kanan, 1991).

The majority of industries are water based and a considerable volume of waste water is discharged to the environment either untreated or inadequately treated leading to the problem of surface and ground water pollution. The capital costs and operating wastewater treatment system are rising on one hand and on the other is pressing demand for the treatment of wastewater generated by increased residential and industrial development. In recent years there has been an increase in alternative and innovative technologies, which will prove to be low cost, low maintenance and energy efficient (Abirami *et al.*, 2005).

Contamination of ground and surface water by different organic pollutants is a major factor of environmental problems for a number of years. Among the organic pollutants, chlorophenols are most common and have been highlighted as priority pollutants by stringent US Environmental Protection Agency (USEPA) (Keith and Telliard, 1979). These pollutants are discharged by the industries into natural water streams and contaminate the ground water (Massa *et al.*, 2004).

Large amount of industrial effluents discharged due to rapid industrialization is a serious pollution threat in our country (Rajula and Padmadevi, 2000). The discharge of effluents contain high temperature, pH, biochemical oxygen demand, chemical oxygen demand, organic pollutants, inorganic pollutants, radioactive materials, total suspended solids and low values

of dissolved oxygen (Arunkumar, 2005). This often represents a risk to the environment (Yapar *et al.*, 2004). The pollutants are toxic to most aquatic organisms, human body and may cause denaturation of protein tissue erosion, paralysis of central nervous system and also damage the kidney, liver and pancreas (Massa *et al.*, 2004; Canpanella *et al.*, 1993).

Rapid urbanization and industrialization with an increased awareness about the need for a clean environment have forced industrialist, environmentalist and government to look for efficient, cheap and lasting solutions to waste treatment and recycling, if complete removal is not possible before their discharge into water streams (Vijayakumar *et al.*, 2005).

### **2.3 METAL POLLUTION**

The term 'heavy metals' refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration (Lenntech, 2004). Heavy metals are a general collective term, which applies to the group of metals and metalloids with atomic density greater than water (Hawkes, 1997).

In recent years, one of the most important global problems is the pollution of the environment by our industrial, economical or social activities (Erdei *et al.*, 2005). According to recent surveys, the most common contaminants reported in ground water are heavy metals (Arpa *et al.*, 2000). The majority of toxic metal pollutants are waste products of industrial and metallurgical processes. Their concentrations have to be reduced to meet ever increasing legislative standards (Kovacevic *et al.*, 2000).

In periodic classification of elements, we have 105 elements. Of these approximately 80 are metals; fortunately out of these 80 metals only 17 metals are toxic. They are Cr, Mn, Fe, V, Co, Ni, Cu, Zn, As, Ag, Cd, In, Sn, Sb, Hg, Ti and Pb (Khopkar, 1998). Major anthropogenic sources of heavy metals include metal extraction, metal fabrication, metal finishing, electroplating, painting, dyeing, surface treatment industry and printed circuit board manufacture (Singh, 2007a; Ajmal *et al.*, 1996). Tremendous increase in the use of heavy metals over a past few decades has inevitably resulted in an increased flux of metallic substances in the environment. The metals are of special concern because of their non-biodegradable nature and persistence in the environment. These heavy metals are very toxic and carcinogenic in nature (Raj, 2004).

The increase in industrial activities, with the release of compounds, has increased environmental pollution and the deterioration of some ecosystems. Unlike organic pollutants, which in most cases can eventually be destroyed, metallic species released into the environment tend to persist indefinitely, circulating and eventually accumulating throughout the food chain thus posing a serious threat to animals and man (Volesky, 1994). According to World Health Organization (1984), the metals of most immediate concern are cadmium, chromium, cobalt, copper, lead, nickel, mercury and zinc.

The water after it is used once for the industrial purpose cannot be reused for the same purpose without treatment. Such water, which emerges out after use from industries is called as the industrial effluent. Such effluents have no definite composition as anything that is not required is carelessly dumped into the stream. Such unwanted disposal material is contributed by chemical firms, food and beverage industries, textile and apparel industries, electronics and electrical material industries or thermal power plants. The quality of such water is characterized by the study of its various physical, chemical and biological properties (Khopkar, 1995).

Toxic heavy metals in air, soil and water are global problems that are a growing threat to the environment. There are hundreds of sources of heavy metal pollution, including the coal, natural gas, paper, and chlor-alkali industries (Alloway, 1995; McDonald and Grandt, 1981). However, roadways and automobiles now are considered to be one of the largest sources of heavy metals (Conservation Currents, 2005). The commonest sources of heavy metal pollution are industrial and mining activities, petroleum exploration, exploitation, processing and effluent management, atmospheric condensation and sewage disposal (Oze *et al.*, 2006).

The presence of heavy metals in the environment is a major concern due to their toxicity. Many industrial processes produce aqueous effluents containing heavy metal contaminants. The environment with the atmospheric depositions of trace metals plays an important role in the biogeochemical cycle of the elements and consequently the contamination of the various ecosystems (Anatolaki and Tsitouridou, 2005).

Electroplating and metal finishing are widely practiced and provide support to many major industries. Electroplating industrial wastes are highly toxic and hazardous chemicals and metals ions, find their way into the effluent (Kokila *et al.*, 2005). Many of the raw materials and chemicals used in the electroplating industry contain toxic substances and thus the waste water contains various heavy metals like Zn, Cu, Fe, Cd, Cr, Ni, Co, Mn and Pb and their presence highly depends upon the type of method used for various industrial purposes (Selvakumari *et al.*, 2002; Prabhakar, 2001).

Nickel and chromium are mostly used in electroplating industries as electroplating baths may contain Cu, Ni, Ag, Au, Zn, Cd, Cr, Sn, Pb, Fe and ammonia (Ghose, 2003). Recent studies indicated that nickel is essential in animal nutrition. Significant concentrations of Ni have been shown to be present in RNA

and DNA. It is associated with the synthesis of Vitamin B-12 (Dara, 2002a). Nickel has been implicated as an embryo toxin and teratogen (Chen and Lin, 1998). The higher concentration of nickel causes poisoning effects like headache, dizziness, nausea, tightness of the chest, dry cough, vomiting, chest pain, shortness of breath, rapid respiration, cyanosis, cancer, dermatitis and extreme weakness (Dara, 2002b; Parker, 1980). World Health Organization has laid stringent standards for nickel concentration in drinking water as 0.1mg/l and industrial effluents as 3mg/l (Dadhich *et al.*, 2004).

Chromium, in the trivalent form [Cr(III)], is an important component of a balanced human and animal diet and its deficiency causes disturbance to the glucose and lipids metabolism in humans and animals. In contrast, hexavalent chromium [Cr(VI)] is a highly toxic carcinogen and may cause death to animals and humans if ingested in large doses (Zayed and Terry, 2003). In India, the permissible limit of Cr(VI) is 0.1mg/l for drinking water, but industrial and mining effluents can be discharged with 0.5mg/l (Baral *et al.*, 2008; Hossain *et al.*, 2005; Chandra *et al.*, 1997). The higher concentration of chromium causes epigastric pain, nausea, vomiting, severe diarrhoea and haemorrhage (Hung and Wu, 1975).

Heavy metals are known toxicants, which inflict acute disorders to the living beings. Electroplating industries pose great threat to the environment through heavy load of metals in the waste water discharged on land and water sources (Jeyanthi and Shanthy, 2007). Heavy metals can pose health hazards if their concentrations exceed allowable limits. Even when the concentration of metal does not exceed these limits, there is still a potential for long term contamination, since heavy metals are known to be accumulative within biological system (Shparyk and Parpan, 2004).

The impact of heavy metal release into our environment is increasing as a result of population explosion, rapid urbanization, industrial and technological expansion, increased energy utilization and waste generation from domestic and industrial sources. These have rendered many waters unwholesome and hazardous to man and other living resources. The release of these heavy metals poses a significant threat to the environment and public health because of their toxicity, bioaccumulation in the food chain and persistence in nature (Ceribasi and Yetis, 2001).

Toxic heavy metal release into the environment has been increasing continuously as a result of man's industrial activities and technological development. The presence of heavy metals such as Cr(VI) and Ni(II) in aquatic systems is of considerable interest because of their cumulative toxicity to aquatic organisms. Industries as well as agricultural and municipal sectors are directly affected by any discharge of these heavy metals into their water sources (Seng *et al.*, 2001).

Widespread concern over the cumulative toxicity and environmental impact of heavy metals has led to extensive research into developing effective alternative technologies for the removal of these potentially damaging substances from effluents and industrial waste waters (Singh, 2007b).

Water pollution due to toxic heavy metals has been a major cause of concern for environmental engineers. The industrial and domestic wastewater is responsible for causing several damages to the environment and adversely affecting the health of the people. Several episodes due to heavy metal contamination in aquatic environment increased the awareness about the heavy metal toxicity (Kumar, 2006). According to recent surveys, the most common contaminants reported in groundwater are heavy metals (Arpa *et al.*, 2000).

### **2.3.1 Chemistry of Heavy Metal Pollution**

Mining activities and other geochemical processes often result in the generation of acid mine drainage, a phenomenon commonly associated with mining activities. It is generated when pyrite ( $\text{FeS}_2$ ) and other sulphide minerals in the aquifer are present and are exposed to air and water in the presence of oxidizing bacteria, such as *Thiobacillus ferrooxidans*, and oxidized to produce metal ions, sulphate and acidity (Ogwuegbu and Muhanga, 2005).

Heavy metals at mining sites are leached and carried by acidic water downstream. They can be acted upon by bacterial and methylated to yield organic forms. This conversion is effected by bacteria in water in the presence of organic matter.

These organic forms have been reported to be very toxic and adversely affect seepage water qualities to pollute underground water sources. Low pH values do not need to be established for metals to be released from mine wastes at adverse concentrations because, near neutral pH (pH 6-7) have been established for metals such as Zn, Cd and As. Factors such as downstream distances from the mining sites, colloid loads, pH perturbations and dilution ultimately control the quality of water sources (Lenntech, 2004).

### **2.3.2 Bio-importance of heavy metals**

Some heavy metals (like Zn, Fe, Ca and Mg) have been reported to be of bio-importance to man and their daily medicinal and dietary allowances had been recommended. Their tolerance limits in drinking and potable water have also been reported. However, some others (like As, Cd, Pb and methylated forms of Hg) have been reported to have no known bio-importance in human biochemistry and physiology and consumption even at very low concentrations can be toxic. Even for those that have bio-importance, dietary intakes have to be maintained at

regulatory limits (Nolan, 2003; Young, 2005). Cr(III) is essential for life, because it participates in different metabolic processes, such as glucose and lipid metabolism in humans and animals (Zayed and Terry, 2003; Baral *et al.*, 2008; Lima *et al.*, 1998). Cr(VI) is toxic. Its toxicity is related to the high oxidation potential of this species and its irreversible reaction with DNA (Lima *et al.*, 1998).

Zinc is a “masculine” element that balances copper in the body and is essential for male reproductive activity (Nolan, 2003). It serves as a cofactor for dehydrogenating enzymes and carbonic anhydrase. Zinc deficiency causes anaemia and retardation of growth and development (McCluggage, 1991).

Calcium is a very vital element in human metabolism. It is the main element in the production of very strong bones and teeth in mammals. Magnesium is an important electrolytic constituent of the blood, present in the blood plasma and body fluids. Arsenic has been reported to be a trace element of nutritional importance to humans but its functions in the biological system is not clear (Holum, 1983).

### **2.3.3 Heavy metal poisoning and biotoxicity**

The biotoxic effects of heavy metals refer to the harmful effects of heavy metals to the body when consumed above the bio-recommended limits. Although individual metals exhibit specific signs of their toxicity, the following have been reported as general signs associated with cadmium, lead, arsenic, mercury, zinc, copper, nickel, chromium and aluminium poisoning: gastrointestinal disorders, diarrhoea, stomatitis, tremor, hemoglobinuria causing a rust-red colour to stool, ataxia, paralysis, vomiting and convulsion, depression, and pneumonia when volatile vapours and fumes are inhaled (McCluggage, 1991). The nature of these effects could be toxic (acute, chronic or sub-chronic), neurotoxic, carcinogenic, mutagenic or teratogenic.

Chromium occurs in natural water in two main oxidation states, Cr(III) and Cr(VI). Although Cr(III) is an essential nutrient in mammalian metabolism, its compounds at high concentrations are both acutely and chronically toxic. Cr(VI) is 500 times more toxic than the trivalent form (Costa, 2003). High concentrations of chromium are toxic to both the plants and animals. Chromium toxicity mostly results from accidental acute poisoning or occupation exposures. Casualties due to chromium toxicity were usually preceded by nausea, vomiting, shock and coma. Occasionally, deaths may occur on account of intravascular haemolysis and acute renal failures (Omkar, 2003).

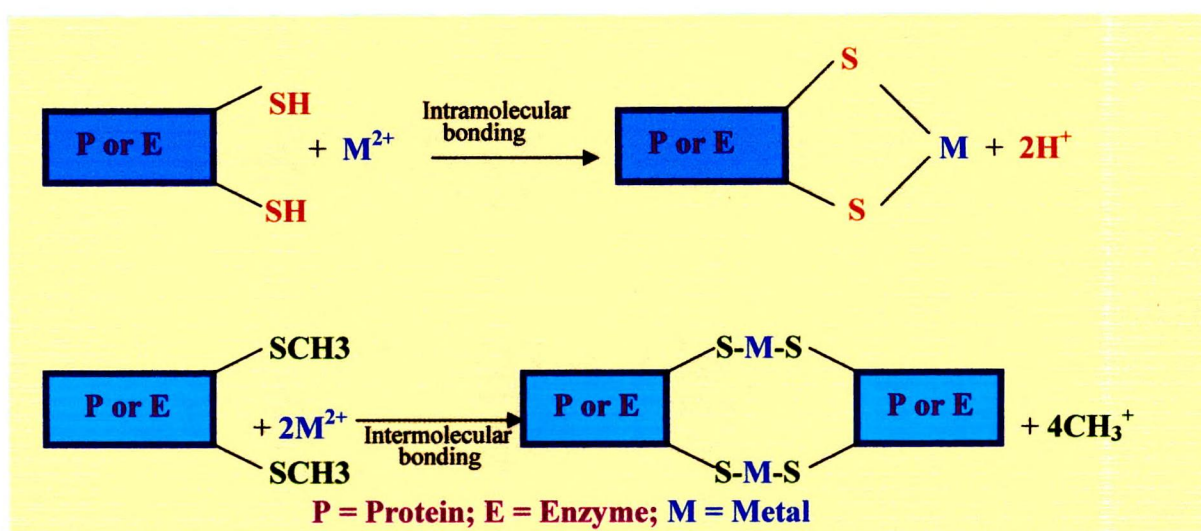
Nickel carbonyl,  $\text{Ni}(\text{CO})_4$  is several times more toxic than CO. The complex breaks down and deposits finely divided nickel in the lungs, which can cause cancer. Initial symptoms of toxicity due to nickel carbonyl are nausea, dizziness, head-ache and chest pain. After 1 to 5 days, severe pulmonary symptoms, tachycardia and extreme weakness develop and even death may occur within 4 to 13 days. Nickel is believed to inhibit various enzymes such as cytochrome oxidase, isocitrate dehydrogenase and malic dehydrogenase (Dara, 2002b).

Cadmium is toxic at extremely low levels. In humans, long term exposure results in renal dysfunction, characterized by tubular proteinuria. High exposure can lead to obstructive lung disease, cadmium pneumonitis, resulting from inhaled dusts and fumes (Young, 2005). Lead is the most significant toxin of the heavy metals and the inorganic forms are absorbed through ingestion by food and water and inhalation (Ferner, 2001). Lead poisoning also causes inhibition of the synthesis of haemoglobin, dysfunctions in the kidneys, joints and reproductive systems, cardiovascular system and acute and chronic damage to the central nervous system and peripheral nervous system (Ogwuegbu and Muhanga, 2005).

### 2.3.4 Biochemistry of toxicity

The poisoning effects of heavy metals are due to their interference with the normal body biochemistry in the normal metabolic processes. When ingested, in the acid medium of the stomach, they are converted to their stable oxidation states ( $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{As}^{2+}$ ,  $\text{As}^{3+}$ ,  $\text{Hg}^{2+}$  and  $\text{Ag}^{2+}$ ) and combine with the body's biomolecules such as proteins and enzymes to form strong and stable chemical bonds (Ogwuegbu and Ljioma, 2003).

**Figure 1. Biochemistry of toxicity**



A metal ion in the body's metallo-enzyme can be conveniently replaced by another metal ion of similar size. Thus  $\text{Cd}^{2+}$  can replace  $\text{Zn}^{2+}$  in some dehydrogenating enzymes, leading to cadmium toxicity. In the process of inhibition, the structure of a protein molecule can be mutilated to a bio-inactive form, and in the case of an enzyme can be completely destroyed (Ogwuegbu and Ljioma, 2003). The most toxic forms of these metals in their ionic species are the most stable oxidation states. In their most stable oxidation states, they form very stable biotoxic compounds with the body's bio-molecules, which become difficult to be dissociated, due to their bio-stabilities, during extraction from the body by medical detoxification therapy.

## 2.4 INDUSTRIAL WASTE WATER TREATMENT

Heavy metals bearing effluent is considered to be hazardous to human life and environment due to their acute toxicity and non-biodegradability even at trace concentrations (Shyamala and Lalitha, 2004). With advancement of science and technology, rapid industrialization is the order of the day. In urban areas all over the world effluents of different industries are the main source of environmental pollution (Shrinivas *et al.*, 1984).

The main goal today is to adopt appropriate methods and to develop suitable techniques either to prevent the metal pollution or to reduce it to acceptable level. There are two options available (1) applications of various methods for removal and / or recovery (2) use of substitutes instead of metallic compounds during manufacturing processes. Second option is in the hands of industrialists. Hence the way to control pollution is to treat the water in the industry itself (Jamode *et al.*, 2003).

However, human activity has pushed the natural purification processes beyond their limits. Therefore, a series of purification operations are required to restore the natural characteristics and life sustaining qualities of water. Water is purified in the following four stages: Preliminary treatment, Primary treatment, Secondary treatment and Tertiary treatment (Sodhi, 2006).

Treatment of aqueous wastes containing soluble heavy metals requires concentration of the metals into a smaller volume followed by recovery or secure disposal. Different treatment techniques have been developed to remove either or both dissolved or suspended heavy metal ions from industrial waters and wastewaters. A number of traditional treatment techniques include precipitation-neutralization, ultra-filtration, reverse osmosis, electrodeposition, solvent extraction, foam flotation, cementation, filtration, evaporation and ion-exchange

(Shyamala *et al.*, 2005; Yurlova *et al.*, 2002; Benito and Ruiz, 2002; Rengaraj *et al.*, 2001). Adsorption on solid matrices is also reported to be a potential method for heavy metal removal (Arpa *et al.*, 2000).

#### **2.4.1 Metal removal by adsorption**

Many physico-chemical methods have been proposed for their removal from industrial effluents (Iqbal *et al.*, 2002). Adsorption plays an increasingly important role in the removal of specific target compounds and classes of compounds from water and waste water (Rathi and Puranik, 2002). Adsorption is an effective purification and separation technique used in industry especially in water and waste water treatments (Al-Ashesh *et al.*, 2000). Adsorption is the exchange of material at the interface between immiscible phases in contact with one another. This process is being mostly employed for removal of dissolved substances from water and waste water (Kannan and Vanangamudi, 1991).

The major advantages of adsorption process for water pollution control are low investment in terms of cost and the adsorbent size having diameters in the range of sub-micron to micron and having large internal porosities to ensure adequate surface area for adsorption. However, the diffusion limitation within the particles leads to a decrease in the adsorption rate and available capacity, particularly for macromolecules such as proteins and DNA. An adsorbent with a high capacity and small diffusion resistance for the adsorption of macromolecules, particularly the biomolecules, would therefore be desirable (Liao and Chen, 2002).

Adsorption techniques among others using a number of organic, inorganic, natural, synthetic, activated or modified model adsorbents are the most widely employed procedures in the waste treatment studies and low cost alternatives or cheaper and effective adsorbents are still needed. Activated carbon, among a large variety of adsorbent, is still the most important one in current use in the

environmental pollution control due to its large surface area, high adsorption capacity, porous structure, selective adsorption on natural polymers and their derivatives are known to remove pollutants from water (Crini, 2005; Ramos *et al.*, 1994).

#### **2.4.2 Bioremediation**

Bioremediation is more economical in many cases and acceptable than other physical and chemical processes because bioremediation results in complete removal of pollutant and its toxicity through metabolic reactions mediated by microorganisms (Gunasekaran, 1999). Bioremediation refers to the process of using microorganisms to remove the environmental pollutants. The microbes serve as scavengers in bioremediation (Sathyanarayana, 2005). Bacteria, fungi, yeast and algae can remove heavy metals and radionuclides from aqueous solutions in substantial quantities (Kapoor and Viraraghavan, 1995).

Bioremediation technologies can be generally classified as *in situ* or *ex situ*. *In situ* bioremediation involves treating the contaminated material at the site while *ex situ* involves the removal of the contaminated material to be treated elsewhere. Some examples of bioremediation technologies are bioventing, land farming, bioreactor, composting, bioaugmentation, rhizofiltration and biostimulation (Neubauer *et al.*, 2000).

For example, heavy metals such as cadmium and lead are not readily absorbed or captured by organisms. The assimilation of metals such as mercury into the food chain may worsen matters (Meagher, 2000). Bioremediation thus involves detoxifying hazardous substances instead of merely transferring them from one medium to another. This process is less disruptive and can be carried out at the site which reduces the need of transporting these toxic materials to separate treatment sites (<http://www.edugreen.ter.res.in/explore/bio/bioreem.htm>).

For bioremediation to be effective, microorganisms must enzymatically attack the pollutants and convert them to harmless products. As bioremediation can be effective only where environmental conditions permit microbial growth and activity, its application often involves the manipulation of environmental parameters to allow microbial growth and degradation to proceed at a faster rate. Most bioremediation systems are run under aerobic, anaerobic and sequential conditions (Sathyanarayana, 2005). Microbes like algae, bacteria and fungi as well as higher plants have capabilities to uptake these pollutants. After uptake, these either accumulate or are assimilated by them. Accumulated heavy metals are recovered for recycling or disposal. *Pseudomonas putida*, *Anthrobacter iscosus* and *Citrobacter* species remove several toxic heavy metals from industrial effluents (Ghose, 2003).

### **2.4.3 Biosorption**

Biosorption is the accumulation of metals without active uptake and can be considered as a collective term for a number of passive accumulation processes which may include ion exchange, coordination, complexation, chelation, adsorption and micro precipitation (Duncan *et al.*, 1994). Other authors (Woodburn *et al.*, 1999) reported that biosorption utilizes the ability of biological materials to accumulate heavy metals from waste streams either by metabolical mediation or by purely physico-chemical pathways of uptake. The uses of biosorption system consist of a biofilm to remove heavy metals with the ability of the activated carbon to remove organic compounds (Scott and Karanjkar, 1995).

The biosorption phenomenon is metabolism independent which involves binding of heavy metals to biomass such as microbial and plant cells. The use of non-living microbial cells as biosorbents has been shown to be an effective means of removal or recovery of heavy metallic species from aqueous systems (Volesky and Holan, 1995). The elimination of a wide range of pollutants and wastes from

the environment is an absolute requirement to promote a sustainable development of our society with low environmental impact. Biological processes play a major role in the removal of contaminants and they take advantage of the astonishing catabolic versatility of microorganisms to degrade / convert such compounds (Neubauer *et al.*, 2000).

The biosorbents can easily be produced using inexpensive growth media or obtained as a byproduct from some industry. The judicious choice of biosorbent can also out compete the commercial ion exchange resins which have conventionally been used in the removal of metals. Microorganisms and microbial products can be highly efficient bioaccumulators of soluble and particulate forms of metals, especially from dilute external solutions and microbe related technologies may provide an alternative or adjunct to conventional techniques of metal removal or recovery. Microorganisms play a significant role in bioremediation of heavy metal contaminated soil and waste water (Congeevaram *et al.*, 2007).

Removal of excesses of heavy metal ions from waste water is essential due to their toxicity. Physico-chemical methods are currently used to remove metals from liquid effluents (Suderman and Oskarson, 1991), but these methods have important disadvantages, such as unpredictable metal ion removal, high reagent requirements and the generation of toxic sludges which are often difficult to dewater and also require extreme caution in their disposal (Kapoor *et al.*, 1999; Gourdon *et al.*, 1990). Cost effective technologies or sorbents for treatment of metal contaminated waste streams are needed (Bailey *et al.*, 1999).

Biological methods such as biosorption / bioaccumulation may provide an attractive alternative to physico-chemical methods for the removal of heavy metal ions (Kapoor and Viraraghavan, 1995).

Alternative metal removal and/or recovery methods being considered are based on metal-sequestering properties of certain natural materials of biological origin (Disimine *et al.*, 1998; Valentine *et al.*, 1996). Certain types of microbial biomass can retain relatively high quantities of metal ions by a passive process, commonly known as biosorption (Volesky, 1990). This process is based on adsorption, ion exchange, complexation and / or micro precipitation (Veglio and Beolchini, 1997). For the industrial application of biosorption, the use of an immobilized biomass in a polymeric matrix or in other supports improves biomass performance and allows its use in many subsequent cycles in the usual unit processes characteristic of chemical engineering (Tsezos, 1988).

Biosorption is a promising alternative, which utilizes inactive or dead biomass to bind and concentrate heavy metals from the aqueous solutions. Different types of biomaterials have shown different levels of metal uptake. Among the most promising biomaterial studies is algal biomass (Vijayaraghavan *et al.*, 2005). A variety of biological materials, especially bacteria, algae, yeasts and fungi have gained considerable significance for heavy metal removal and recovery due to their good performance, low cost and large available quantities (Volesky, 1990).

Biosorption is possible by both living and non-living biomass; however, bioaccumulation is mediated only by living biomass. Further, bioaccumulation is growth independent and microbial biomass can be used and exploited more effectively for biosorption rather than accumulation (Gupta *et al.*, 2000).

The success of heavy metal removal depends on the binding properties of the selected biomass and on metal chemistry in the solution under the given process conditions. The biomass cell walls, which are the sites of primary contact with the solution, act as the main heavy metal-binding surfaces (Zhang *et al.*, 1998). Their complex structure (Siegel *et al.*, 1990) represents an extensive

network of heterogenous binding mechanism which includes electrostatic binding and / or complexation to the active groups on the microbial surface (Brady and Tobin, 1995). This can be subsequently followed by further deposition of metal onto already adsorbed ions (Zhang *et al.*, 1998; Tsezos and Volesky, 1982).

Different types of biomaterials have shown different levels of metal uptake. Algal surfaces (cell wall / mucilage) have been found containing different functional groups such as carboxyl, hydroxyl, sulphate and other charged groups, which are created by their carbohydrate, protein and lipid components and are believed to be responsible for impressive metal uptake (Iman *et al.*, 2008). Mycelial wastes of microbial origin from fermentation industries have been recognized as potential biosorbents for decontamination of waste waters containing heavy metals (Puranik and Paknikar, 1997). The fungal mycelium pellets of *Aspergillus niger* 405 were used for adsorption of different metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{CrO}_4^{2-}$  (Kovacevic *et al.*, 2000).

Based on the critical analysis of various microbial biomasses, a few potent metal sequestering biosorbents have been commercialized. The performance of biosorbent can further be improved by various physical and chemical treatments. The pretreatments modify the cell surface either by removing or masking the groups or exposing more metal binding sites. Various commercial microbial biosorbents available are AlgaSorb, AMT-Bioclaim and Bio-fix. The economics of these sorbents merit their commercialization over chemical ion exchangers (Gupta *et al.*, 2000).

A potent algal biosorbent AlgaSorb was developed using the fresh water algae *Chlorella vulgaris* to treat waste water (Darnell *et al.*, 1986). It was found to efficiently remove metallic ions from dilute solutions and its performance was not affected by the presence of calcium and magnesium ions. Another metal sorption agent AMT-Bioclaim (MRA) employed *Bacillus* biomass to manufacture

granulated material for wastewater treatment and metal recovery. This was found to accumulate metal cations with efficient removal of more than 99% from dilute solution. Bio-fix biosorbents use biomass from a variety of sources including *Cyanobacterium (Spirulina)*, yeast, algae and plants. Metal binding to these adsorbents was recorded to be approximately four fold higher than the ion exchange resins (Diels *et al.*, 1993).

## 2.5 METAL SORPTION

Adsorption processes is the most widely used method and offers a relatively simple method for the removal of metals. Adsorption on activated carbon is also an expensive method for the treatment of industrial effluents and is wide popular in developed countries. Many adsorbent materials have been evaluated for low cost operation and high efficiency (Katyal *et al.*, 2003).

The use of agricultural products and by-products has been widely investigated as a replacement for current expensive methods of removing heavy metals from water and wastewater. Some of the agricultural materials can be effectively used as low-cost sorbents. Modification of agricultural by-product could enhance their natural capacity and add value to the by-product (Kumar, 2006).

Some of the low cost adsorbents used to remove heavy metals are coal fly ash (Gupta and Singh, 2004), fly ash (Cho *et al.*, 2005) and agricultural waste materials like pea nut hull (Johnson *et al.*, 2002; Zacardia, 2002), bagasse (Rao *et al.*, 2003; Mohan and Singh, 2002; Khan *et al.*, 2004; Gupta *et al.*, 1999; Garg *et al.*, 2007), hazel nut shell (Cimino *et al.*, 2000), jack fruit, soy bean hull (Babel and Kurniawan, 2003), eucalyptus bark (Sarin and Pant, 2005), jack fruit peel (Inbaraj and Sulochana, 2004), rice husk (Chuah *et al.*, 2005; Dadhich *et al.*, 2004; Khan *et al.*, 2004), olive mill residues (Veglio *et al.*, 2003), papaya wood (Saeed *et al.*, 2005a), groundnut shell and saw dust (Shukla and Pai, 2005), tires and saw

dust (Hamadi *et al.*, 2001), peanut husks, cassava waste (Harsfall and Abia, 2003), sago waste (Quek *et al.*, 1998), coconut tree saw dust, maize, cob, banana pith, silk (Khan *et al.*, 2004), cotton hull (Kadirvelu *et al.*, 2003), orange waste (Dhakal *et al.*, 2005; Satpute *et al.*, 2005), oil palm shell (Guo and Lua, 2002; Nomambhay and Palanisamy, 2005), tea waste (Mahvi *et al.*, 2005), corn cobs, corn starch, pine bark (Zacardia, 2002) and modified peat resin particles (Sun *et al.*, 2004).

Selected microorganisms were used to remove metal ions like *Spirogyra species* (Singh, 2007a), *Pantoea sp.* (Ozdemir *et al.*, 2004), *Streptoverticillium cinnamoneum* (Puranik and Paknikar, 1997), *Brevibacterium sp.* (Taniquchi *et al.*, 2000), *Rhizopus nigricans* (Kogej and Pavko, 2001), *Aspergillus niger* (Kovacevic *et al.*, 2000), *Pseudomonas fluorescens* (Lopez *et al.*, 2002), *Pseudomonas putida* (Chen *et al.*, 2005), *Chlorella vulgaris* (Aksu, 2002), *Chlorella vulgaris* and *Chlorella miniata* (Lau *et al.*, 1999), *Rhizopus oligosporus* (Ariff *et al.*, 1999), *Rhizopus arrhizus*, *Mucor miehei* and *Penicillium chrysogenum* (Fourest *et al.*, 1994) and *Oscillatoria species* (Singh, 2007b) as adsorbents for the removal of metal ions.

Some of the animal waste materials like hen egg shell membrane, wool, silk (Goto and Suyama, 2000), chicken feather (Al-Asheh *et al.*, 2002; Goto and Suyama, 2000; Sayed *et al.*, 2005), sheep manure materials (Kandah, 2001), human hair (Banat and Al-Asheh, 2001), animal horns (Banat *et al.*, 2002), low rank Turkish coals (Karabulut *et al.*, 2000), bone char (Choy and McKay, 2005), modified coir fiber (Kar and Misra, 2004), kyanite (Ajmal *et al.*, 2001), calcite and hydroxyapatite (Rio *et al.*, 2004), calcined phosphate (Akhil *et al.*, 2004), crushed concrete (Coleman *et al.*, 2005), carbon aerogel (Meena *et al.*, 2005), bentonite (Ulmanu *et al.*, 2003; Kaya and oren, 2005; Banat *et al.*, 2000), diatomite (Ulmanu *et al.*, 2003), modified jute fibres (Shukla and Pai, 2005), Turkish fly ash (Bayat, 2002) and purified carbon nano tubes (Lu and Chiu, 2006) were used to remove metal ions present in the waste water.

## 2.6 HUMAN HAIR AS AN ADSORBENT

Scalp hair has been used as early as 1929 to assess human systemic levels of elements. Hair is widely accepted for assessing toxic element exposures and measured by most clinical laboratories capable of making trace element measurements. Using hair to assess essential elements is more controversial, yet researchers have found many correlations of essential elements to diseases, metabolic disorders, environmental exposures and nutritional status (Katz and Chatt, 1988; Man *et al.*, 1996; Bass *et al.*, 2001).

Human hair waste was tested as an adsorbent for the removal of phenol from aqueous solutions. Upto 92% phenol removal was achieved from aqueous solutions. The initial pH of the solution had a strong effect on the uptake of phenol and increasing the measurement temperature also increased the uptake (Banat and Al-Asheh, 2001). The use of human hair to remove heavy metal ions from domestic and industrial waste water to safe levels has been recommended as a cheap and effective alternative for commercial ion exchange resins.

## 2.7 ADSORPTION ISOTHERM

To determine the adsorption capacity of the new adsorbent material, a study of adsorption isotherm is essential and is helpful in selecting the adsorbent for the removal of metal ion at a particular concentration (Deo and Ali, 1992).

In general, the adsorption isotherm describes how adsorbates will interact with adsorbents and so is critical in optimizing the use of adsorbent. Adsorption data for wide range of adsorbate concentrations are most conveniently described by adsorption models, such as Freundlich or Langmuir isotherm, which relate adsorption density  $q_e$  (uptake per unit weight of adsorbent) to equilibrium adsorbate concentration in the bulk fluid phase,  $C_e$ . The adsorption models have

been used to determine the mechanistic parameters associated with the adsorption process (Jain *et al.*, 2008).

Two widely accepted adsorption isotherm models linearized Freundlich and Langmuir models. These isotherms are used to analyse the equilibrium data for the removal of heavy metals using low cost adsorbents (Rao and Bhole, 2001).

The Freundlich equation has been widely used and is applicable for isothermal adsorption. This is a special case for heterogeneous surface energies in which the energy term,  $b$ , in the Langmuir equation varies as a function of surface coverage,  $q_e$ , strictly due to variations in heat of adsorption. The logarithmic form of Freundlich equation is represented as:

$$\begin{aligned}\text{Log } x/m &= \text{log } k_f + 1/n \text{ log } C_e \quad (\text{or}) \\ \text{Log } q_e &= \text{log } k_f + 1/n \text{ log } C_e\end{aligned}$$

where,

$x$  is the mass adsorbate absorbed

$m$  is the mass of the adsorbent

$q_e$  is the amount adsorbed

$C_e$  is the equilibrium concentration of the adsorbate ions.

$k_f$  and  $n$  are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. When  $\text{log } q_e$  is plotted against  $\text{log } C_e$ , a straight line with slope  $1/n$  and intercept  $\text{log } k_f$  is obtained (Jain *et al.*, 2008; Singh, 2007a).

Langmuir's isotherm model suggests that uptake occurs on homogeneous surface by monolayer sorption without interaction between sorbed molecules. The linear form of Langmuir isotherm equation is represented by the following equation:

$$C_e/q_{eq} = 1/Q_{max}b + C_e/Q_{max}$$

where,

$q_{eq}$  is the amount of metal sorbed per unit dry weight of sorbent at equilibrium (mg/g)

$C_e$  is the residual metal ion concentration left in solution after binding

$Q_{max}$  is the maximum possible amount of metallic ion sorbed per unit weight of sorbent and

$b$  is the equilibrium constant related to the affinity of the binding sites for the metal ions (Singh, 2007b).

Sharma and Bhattacharyya (2004) observed that Cr(VI) sorption on neem leaf powder followed both Freundlich and Langmuir isotherms, which showed that neem leaf powder has an adsorption capacity much larger than those reported in the literature for non-conventional and low cost adsorbent.

Shukla *et al.*, (2006) observed the value of  $1/n$  less than 1 in their adsorption studies with modified coir fibres for the removal of Ni(II), Zn(II) and Fe(II), which indicated a favorable adsorption.

Based on the above literature, the present study was aimed to assess and evaluate the adsorption capacity of powdered human hair to remove nickel(II) and chromium(VI) from synthetic metal solutions of known concentrations of nickel(II) and chromium(VI) at selected experimental conditions.