Chapter 1

Introduction

Man’s progress depends on his capacity to understand nature and harness its resources. On contrary, in his mad race for development, man has been ruthlessly consuming ‘natural resources’ and causing pollution to the environment. Pollution is a general term which refers to the movement of pollutant/toxic substances through environment. The pollutant/toxic substances are the ones which cause deleterious effect on the environment. In its natural uninterrupted condition, the environment of any region is in the state of dynamic equilibrium (Balance of nature) and it is only when human exploit and interfere with nature, this equilibrium is destroyed. As a result of rapid industrialization in the last few decades, the emergence of different pollutants, inclusive of toxic metals, have greatly disturbed the delicate balance of nature causing detrimental effect to human kind and other living organism.

1.1 HEAVY METALS

“Heavy metal” is a general communal term assigned to the collection of metals and metalloids having atomic density greater than 4000 kg/m$^3$ and specific gravity greater than five (Garbarino et al., 1995). They are the natural component of earth crust. Most of the heavy metals other than cadmium, mercury and lead are essential micro nutrients needed for living beings at lower concentration, but at higher concentration they can lead to severe poisoning.

1.2 CHROMIUM

Chromium (Cr) is the seventh most abundant transition metal element occurring naturally on earth. It was first discovered in the year 1797 by a French chemist, Nicholas Louis Vauquelin at the Paris Ecole Des Mines from a Siberian red lead ore (crocoite). A yellow pigment (chromium) produced from crocoite was the first commercially used chromium for paint production. The name “Chromium” was derived from a Greek word “Chroma” meaning colour. Chromium was then discovered in commonly occurring mineral chromite from the Ural Mountains.
The major commercially traded forms of chromium materials include chromite ore and ferrochromium (a product of smelted chromite ore). Globally about 77% of known resources are from South Africa and are also found in other parts of the world like Kazakhstan, Zimbabwe, Finland, India, Brazil, Turkey, Albania, Russia, United States and Iran. Based on geological survey of statistics, India is one among the largest producers of chromite ore in 2009 with greater contribution from Orissa (Sukinda mines) and remaining from the states of Karnataka and Maharashtra.

1.2.1 GENERAL CHARACTERISTICS OF CHROMIUM

<table>
<thead>
<tr>
<th>Category</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name, symbol</td>
<td>Chromium (Cr)</td>
</tr>
<tr>
<td>Atomic Number</td>
<td>24</td>
</tr>
<tr>
<td>Atomic Mass</td>
<td>51.9961 amu</td>
</tr>
<tr>
<td>Metallic category</td>
<td>Transition metal</td>
</tr>
<tr>
<td>Melting Point</td>
<td>1857.0 °C (2130.15 K, 3374.6 °F)</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>2672.0° C (2945.15K, 4841.6° F)</td>
</tr>
<tr>
<td>Density @ 293 K</td>
<td>7.19 g/cm³</td>
</tr>
<tr>
<td>Colour</td>
<td>Grey</td>
</tr>
</tbody>
</table>

Table 1.1 presents the details of basic information on chromium. Chromium from chromite ore exists in a wide range of oxidation states (0, +1, +2, +3, +4, +5 and +6). Of the valence states of chromium, the stable and most occurring forms include Cr(0), Cr(+6) and Cr(+3). Elemental chromium (Cr(0)) is a lustrous steel grey metal that does not occur naturally but is used for making steel (ATSDR, 2012). The other valence states like Cr(+5) and Cr(+4) sometimes form unstable intermediates in the conversion of Cr(+6) to Cr(+3).
1.2.2 HEXAVALENT CHROMIUM

Cr(VI) exists in aqueous environment as water soluble ions and considered as an eighteenth toxic priority pollutant (ATSDR, 2012). It is a strong oxidizing agent which gets reduced by organic matter or reducing agents to form trivalent chromium. The ground state electronic configuration of the chromium atom is: 1s\(^2\) 2s\(^2\)2p\(^6\) 3s\(^2\)3p\(^6\) 3d\(^5\)4s\(^1\). The most probable Cr(VI) exists in solution as chromic acid (H\(_2\)CrO\(_4\)) or as oxyanions of chromate (CrO\(_4^{2-}\)), bichromate (HCrO\(_4^{-}\)) and dichromate (Cr\(_2\)O\(_7^{2-}\)) (Gheju, 2011). The existence in different forms in aqueous solution mainly depends on the pH of the solution, Cr(VI) concentration and the redox potential (Cespón-Romero et al., 1996). The acid anhydride (CrO\(_3\)), the acid chloride (CrO\(_2\)Cl\(_2\)), different metal chromates (MCrO\(_4\)) and metal dichromates (MCr\(_2\)O\(_7\)) are typical hexavalent chromium compounds. Chromates are yellow and dichromates are orange in colour.

1.2.3 TRIVALET CHROMIUM

Cr(III) is less toxic and less soluble in water. The electronic configuration of trivalent chromium is: 1s\(^2\) 2s\(^2\)2p\(^6\) 3s\(^2\)3p\(^6\)3d\(^3\). It can be readily precipitated from the solution in the form of Cr(OH)\(_3\). Trivalent chromium exists as [Cr(OH\(_2\))\(_6\)]\(^{3+}\) under pH lesser than 3.6 and as solid Cr(OH)\(_3\) above 6.5 pH (Gheju, 2011).

1.3 USES OF CHROMIUM

Chromite, an only economic source of chromium has wide range of application in metallurgical, chemical and refractory industries because of its important properties such as resistance to corrosion, oxidation, wear and galling and hardenability.

1.3.1 METALLURGY INDUSTRY

Chromium is mainly used in metallurgical industries as an alloying element with iron to make oxidation resistance stainless steel (Iron- Chromium alloy). The common uses of stainless steel include machinery, containers and pipes in industries and as kitchen products. The production of non-ferrous alloy is also an important application of chromium in metallurgical industry.
1.3.2 REFRACTORY MATERIAL

Chromite mineral is used directly by the refractory industry to produce bricks (blast furnaces, cement kilns, moulds for the firing of bricks, foundry sands (for casting of metal) for metallurgical and high-temperature industrial mineral processing industrial applications. Due to its high temperature, sapling, corrosion and abrasion resistant properties, chromium find application as the refractory material.

1.3.3 CHEMICAL INDUSTRY

Chrome-based chemicals exist in hexavalent and trivalent forms (chromic anhydride, chromium trioxide, chromium sulfate, chromium chloride) and are used in electroplating industry for chrome plating. Chrome plated objects are used for decorative, corrosion resistance and ease maintenance purposes. Copper dichromate is widely used as a wood preservative to protect from decay by fungi and wood attacking insects (termites). Chromium sulfate, Cr(III) salts and chrome alums are used in leather industry in tanning of leather for enhancing the stability by cross linking the collagen fibers.

Lead chromate (PbCrO₄) (Chrome yellow) has been used as yellow pigments in paints. Chromic oxide (Cr₂O₃), also known as chrome green, is a widely used green pigment. The other chromium compounds are used as mordant, which permanently fix dyes to fabrics. Chrome-metal based dyes are used as textile and leather dyes. Chromium chemicals are used as catalysts for processing hydrocarbons. For example, mixtures of chromium and silicon dioxide/chromium, titanium and aluminium oxide are used for the production of polyethylene.

1.4 CHROMIUM CONTAMINATION IN ENVIRONMENT

Chromium append into air, soil and water in the following ways:

- Anthropogenic activities of industries such as electroplating, leather tanning, dyes and pigments, textile, metallurgical, refining and chrome based chemical manufacturer
- Burning of natural gas, oil and coal
Improper disposal of mine water from underground and open pit mines

Leachate from solid waste dumps

Chromium pollution in the form of Cr(VI) in atmospheric is mainly removed by plunge out and precipitation with the resistance time of less than 10 days. Hence most of chromium is deposited in water (surface and ground water) and soil sediments (Gheju, 2011).

Chromium contamination in many countries is generally caused by leather tanning industries. 160,000 metric tons of chromium per year in US (Cabeza et al., 1998; Brindha and Elango, 2012) and 54 kg of chromium/day in India (Brindha and Elango, 2012) are reported to be generated from US and Indian tanneries respectively. Tannery industrial development is one among the main reason for chromium pollution in India. Though Cr(III) sulfate is used in leather tanning, Cr(VI) is generated due to post tanning processes. Irrespective of strict regulation for treating effluent by common effluent treatment plants, efficiency is not up to the mark to meet the effluent standard recommended by central pollution control board. Ramteke et al (2010) reported that the concentration of Cr(VI) (5.48 mg/l) after treatment by the Common Effluent Treatment Plant (CETP) exceeded the recommended standard value (Inland surface water discharge is 2 mg/l (CPCB, 2008)).

Based on Indian central pollution control board report (unpublished report), the highly chromium contaminated site in India include: Ranipet (Tamil Nadu) followed by Kanpur (Uttar Pradesh), Vadodara (Gujarat) and Talcher (Orissa). Out of 1200 tanneries (approx.) in India, Tamil Nadu accounts for more than 75 %. Ranipet in Vellore district is a medium–sized community located about 100 miles from Chennai and is found to be the world’s fifth largest polluted area. Vast agricultural lands in this region are uncultivable due to pollution. Soil surrounding tannery industries are severely contaminated with chromium concentrations above the maximum threshold limit. The chromium concentration in ground water and surface water are also recorded higher than the recommended limits, compared to other parts of India. Gowd and Govil (2008) reported that chromium levels in surface water in the industrial region of Ranipet were in the range of 2.4 to 1,308.6 µg/l (average of 247.2 µg/l).
Apart from tanneries and leather finishing industries located in the vicinity, a chromate factory (Tamil Nadu Chromates & Chemicals Ltd (TCCL)), which is not functioning at present, produced sodium chromate, chromium salts and basic chromium sulfate. Solid waste dump (150,000 tons) rich in chromium with other pollutant, accumulated over two decades (Rao et al., 2011). Though the factory is closed, the leachate from the improper disposal has been polluting the ground water in the downstream areas of TCCL premises and levels of Cr(VI) in ground water are exceeding the permissible levels (Sankaran et al., 2010; Rao et al., 2011). The chromium level in the ground water was reported to be 275 mg/l (Rao et al., 2011) in the same TCCL area. The concentration of total chromium in the wells near to TCCL varies between 3.1 to 246 mg/l whereas the concentration of hexavalent chromium varies between 2.1 to 214 mg/l which exceed the concentration of 0.05 mg/l prescribed under Indian Standards Specification for Drinking water quality (CPCB, 2008). The ground water in these areas, is therefore, severely contaminated with hexavalent chromium.

Notably there are several other contaminated sites due to tanneries are located in other parts of Tamil Nadu like Chrompet in Chennai, Ambur and Vaniampadi on the banks of the Palar river (apart from Ranipet) and few in Dindigul and Erode. A study conducted by Brinda and Elango (2012) on ground water pollution caused by tanning industries in Chrompet area revealed that the concentration of chromium was above the permissible limit (0.05mg/l) in 86% of the ground water samples. Kumar and Riyazuddin (2011) reported chromium speciation in ground water around tanneries in Chrompet. Cr(VI) concentration ranged from 32.50 and 200.30 µg/l with a mean value of 55.27 µg/l. Mondal et al (2005) indicated that ground water in Dindigul area is heavily polluted due to tannery effluent. Distribution of chromium in soil, surface water and ground water (Ramasamy et al., 2000) in vicinity of Ambur and Vaniampadi were also reported to be higher than the permissible limit.

Apart from chromium pollution, the tannery effluents confer specific characteristics to the environment (soil, ground and surface water). The general characteristics of tannery waste is distinguished by its high NaCl and other heavy metals like Cd, Pb, Cu, Fe, Mn, Ni and Zn (Ramteke et al.,2010). Gowd and Govil (2008) reported that the surface water in the area of Ranipet leather industrial area is
highly contaminated with high concentrations of toxic metals like Cadmium ranging from 0.2 to 401.4 µg/l (average of 51.1 µg/l), Chromium 2.4–1,308.6 (average of 247.2 µg/l), Copper 2.1–535.5 µg/l (average of 95.5 µg/l), Nickel 1.6–147.0 µg/l (average of 36.7 µg/l), Lead 6.4–2,034.4 µg/l (average of 467.8 µg/l) and Zinc 20.8–12,718.0 µg/l (average of 3,760.4 µg/l). High levels of chromium, manganese, nickel and zinc in the post treated tannery effluent at CETP reported by Ramteke et al (2010) shows the contribution of other heavy metal pollution by untreated or less efficiently treated tannery effluents. The same reports by Ramteke et al (2010) shows that sodium salts are added to the environment without removal (sodium ion in untreated effluent = 4090 mg/l and Treated effluent = 4190 mg/l). Sodium chloride is one of the major chemical used in the tanning industry for preserving the raw materials apart from sodium sulphide which is used during liming process (Brinda and Elango, 2012). Studies on the impact of tanning industries on ground water of chrome pet revealed that the concentration of sodium salts was found to be between 91 mg/l and 499 mg/l exceeds the World Health Organization (WHO) permissible limit of 200 mg/l (Brinda and Elango, 2012). The chloride ion in the same vicinity was above the desirable limit of 250 mg/l with alkaline pH revealing the same characteristics of treated effluents (Brinda and Elango, 2012). Mondal and Singh (2011) reports on geophysical survey on the industrial belt (with 80 functional leather factories in southern India on shallow ground water) showed ranges of Na⁺ and Cl⁻ ions that were from 46 to 4,850 mg/l (mean, 348 mg/l) and 25 to 10,390 mg/l (mean, 1,079 mg/l), respectively. The total dissolved solids (TDS) and chloride contents in the open wells in the tannery cluster varied from 27,686 to 39,100 and 12,000 to 13,652 mg/l, respectively (Mondal and Singh, 2012). Thus in addition to Cr(VI) pollution, tannery effluents affected area showed increase in the level of TDS, sodium and chloride ions and other toxic heavy metals.

In addition to chromium pollution contributed by tannery industries, textile industries in Tirupur and textile and electroplating industry in Coimbatore have been reported to contribute to metal pollution in Tamil Nadu (Govindarajalu, 2003). Open wells and bore wells in and around Tirupur and downstream of Noyyal exhibited high levels of TDS, chloride, heavy metals (zinc, chromium, copper and cadmium) in ground water (Govindarajalu, 2003). Noyyal River flowing in Coimbatore, Erode and Karur districts are also heavily polluted with metal ions and NaCl salts. The metal and
salt pollution is due to high levels of NaCl and metal based dyes used in textile processing units (Govindarajalu, 2003).

In summing up, Tamil Nadu especially Ranipet industrial area is heavily polluted with toxic hexavalent chromium expecting urgent need for remediation. However the remediation would be a challenging one, as along with chromium soil, surface and ground water are heavily affected by salinity and other toxic metals.

1.5 CHROMIUM AS A MICRONUTRIENT

On comparison between the most stable chromium oxidation states, Cr(III) is less toxic than Cr(VI). Moreover Cr(III) is a vital micronutrient for normal metabolism (Thacker et al., 2006). When Cr(III) exist in its biologically active form (glucose tolerance factor (GTF), a dinicotinato chromium [III] glutathione-like complex) and it facilitates the interaction of insulin with its receptor site influencing glucose, protein, and lipid metabolism (US EPA, 1998). Thus, Cr(III) is considered essential for animals and human beings. The recommended intake for adolescents and adults ranges between 20- 45 µg of chromium(III) per day (ATSDR, 2012). Studies have shown that chromium supplementation (Brewer's yeast, chromium(III) picolinate and inorganic trivalent chromium) in deficient patient can result in improved glucose, protein, and lipid metabolism (ATSDR, 2012). Though Cr(III) is considered as an essential element, Cr(III) deficiency reports in human are not reported (ATSDR, 2012).

1.6 TOXICITY OF CHROMIUM

Hexavalent chromium is highly toxic than other chromium species and is regarded as the possible human carcinogen (US EPA, 1998). The route of exposure of any chromium species includes (a) Inhalation (b) Ingestion and (c) Dermal contact (US EPA, 1998). On oral inhalation, insoluble forms of chromium enter lungs and linger for several years and it occurs due to the occupational exposure by breathing contaminated air. Dermal entry of Cr(III)/Cr(VI) can occur only when skin is damaged leading to minor exposure to general population. Oral ingestion is the predominant route of exposure to general population (US EPA, 1998). The kinetics of orally ingested chromium compound depends on its valence state and its ligand.
Hexavalent chromium species is absorbed more readily than the trivalent chromium species in insoluble (CrCO$_3$) as well as in soluble form (CrCl$_3$). As a natural mechanism, certain percentage of ingested Cr(VI) enters into the body through digestive tract and gets converted in stomach into insoluble Cr (III) which in turn reduces the absorbance level of toxic chromium (ATSDR, 2012). The other absorbed chromium distributes itself into various regions of body like tissues, kidney, liver and bone. When exposed to higher level of chromium, as an alarming act high level of chromium is articulated in blood, urine, expired air, hair and nails and are considered as biomarkers for chromium contact (ATSDR, 2012).

On health aspects, the vulnerable targets of Cr(VI) include respiratory tract, gastrointestinal and the reproductive system (US EPA, 1998). The high level of respiratory inhalation leads to nasal irritation and breathing problems like asthma and wheezing. The stomach and intestine exposed to Cr(VI) showed high level of irritation and abrasion leading to ulcer development, internal bleeding, necrosis and bloody diarrhea. The male reproductive system is affected by decrease in sperm count and damage.

Accidental/deliberate oral consumption of Cr(VI) has confirmed hematological effect leading to anemia followed by hemorrhage (US EPA, 1998). Extreme consumption affects the respiratory, cardiovascular, gastrointestinal, hematological, renal, neuron system and might ultimately lead to death (ATSDR, 2012). Cr(VI) is also considered as mutagenic as they are demonstrated to produce genotoxic adducts in the presence of glutathione causing inhibition to DNA replication (US EPA, 1998). Industrial exposure and animal studies specify that breathing and oral exposures to chromium(VI) compounds are coupled with respiratory and gastrointestinal system cancers, respectively. Hence Cr(VI) is classified to be human carcinogen compound by the International Agency for Research on Cancer (IARC) (ATSDR, 2012).

With exception of occupational exposure, general population living in the vicinity of contaminated site also experience drastic health effect due to consumption of chromium contaminated agricultural products and water. Gowd and Govil (2008) reported occupational diseases such as asthma, chromium ulcers and skin diseases in people who were working in Ranipet leather industry.
1.7 Cr(VI) REGULATION

Based on health aspects and levels of toxicity reported, prevalence of Cr(VI) more than the permissible limit in aquatic bodies is considered as a health alarm for living beings. Hence strict rules and regulation have been implemented by various organizations. The World Health Organization (WHO) recommended maximum allowable limit for hexavalent chromium and total chromium in drinking water include 0.05 and 2mg/l, respectively (Gupta et al, 2011). The maximum tolerance limit recommended by central pollution control, India on drinking water for Cr(VI) is 0.05 mg/l (CPCB, 2008). Hence remediation or treating the chromium contaminated environment becomes indispensable.

1.8 TREATMENT METHODS

The treatment methods for chromium remediation include physico-chemical methods that include either removal of toxic hexavalent chromium directly or reduction of hexavalent chromium to non toxic trivalent chromium followed by precipitation.

1.8.1 REMOVAL OF CHROMIUM

1.8.1.1 ADSORPTION METHODS

Adsorption methods are widely used to remove chromium from contaminated water. The main principle involved is sorption of metal onto the pores of the sorbent from the bulk liquid which reduces the concentration of toxic metal in the liquid media. The different types of adsorbent materials used are activated carbon, biosorbents and industrial waste sorbents.

1.8.1.1.1 ACTIVATED CARBON

The widely considered adsorbent materials are the activated carbon prepared from different sources to suit a wide variety of conditions. Uses of coconut shell and wood (Selomulya et al., 1999; Owlad et al., 2009) and rubber wood saw dust (Owlad et al., 2009) have been reported. The advantage of activated carbon is because of its high surface area (500 to 1,500 m²/g) (Owlad et al., 2009). It is widely prepared in
different sizes and shapes. They have classified as granular activated carbon (GAC) and powdered activated carbon (PAC). The adsorption capacity reported for few commercially available activated carbon include: F-400 (Hamadi et al., 2001), SHT and GA-3 (Hu et al., 2003).

Adsorption has several advantages like low price and easy operation over other conventional methods. However, the high adsorption capacity depends on its pH (low pH) and salinity (low salinity) which is not usually suited for removal of Cr(VI) from saline water. Moreover several activated carbons do not directly suit to remove Cr(VI) under different physicochemical conditions and needs to be chemically activated to enhance its adsorption capacity (Mohanty et al., 2005; Owlad et al., 2009). The other main demerit includes it’s desorption and regeneration capacity, otherwise toxic Cr(VI) would be disposed to append as leachate.

1.8.1.1.2 BIOSORPTION

Biosorption is proven as new and promising process in the removal of Cr(VI) from effluent water. In general, adsorbent material for biosorption is the agricultural waste or its byproducts. Eg: Pine needles and Cactus (Dakiky et al., 2002) and Hazlenut shell (Cimino et al., 2000). The mechanism involved in biosorption is a complex process that involves chemisorption, complexation with adsorption on surface and pores and ion exchange (Gardea-Torresdey et al., 2004; Owlad et al., 2009). The advantage of using this method is its low cost, less sludge production, no nutrient requirement and recovery of metals (Owlad et al., 2009). The disadvantage include its high consideration with change in pH, ionic strength, ligands (organic/inorganic) and thus making it not always suitable for varying field operation (Owlad et al., 2009). Moreover, plant material cannot be directly used without chemical treatment (acid or base components), as they would release soluble organic compounds that leads to rise in Biological Oxygen Demand (BOD), Chemical oxygen demand (COD) and Total Organic Carbon (TOC) (Gaballah et al., 1997; Owlad et al., 2009).
1.8.1.3 INDUSTRIAL WASTES SORBENTS

Industrial waste generally disposed as solid waste is used as sorbents for removing chromium. Iron(III)hydroxide from fertilizer industries (Namastivayam and Ranganathan, 1993), Blast-furnace slag from steel plants (Srivastava et al., 1997) and Chitin, a exoskeleton waste from crab meat canning industry (Udaybhaskar et al., 1990) are a few examples studied for its application as adsorbents. Though these sorbents are extremely cost effective, they are non porous sorbents and sorption capacity depends on its medium pH (Owlad et al., 2009).

1.8.1.2 ION EXCHANGE METHOD

Ion exchange is a unit operation by which ions of a specific species are displaced from an insoluble exchange material by ions of a different species in solution. The Chromium ion containing solution enters at one end of the column under pressure and passes through the resin bed where chromium is removed from the solution. When resin capacity is exhausted, the column is backwashed to remove trapped solids and then regenerated Eg: Dowex 2-X4 (Sapari et al., 1996), Ambersep 132 (Lin and Kiang, 2003) and Solvent impregnated resin with aliquat 336 (Kabay et al., 2003). Though this method is energy efficient with low maintenance, it has to be pointed out that it’s very selective, costly and easily fouled by organics and other solids from wastewater. In general waste water with high suspended solids and salts has to be pretreated before treating it with ion exchange resin thereby limiting its application with selected industrial waste water.

1.8.1.3 MEMBRANE FILTRATION

Membrane filtration by inorganic, polymeric and liquid membranes has received significant attention to remove Cr(VI) from waste water. Modified ultrafiltration carbon membrane (Pugazhenthi et al., 2005) by gas phase nitration (using NOx) and amination (using hydrazine hydrate); ceramic membranes containing ion-exchange component (Dzyazko et al., 2007) has been reported for inorganic polymer. The inorganic membranes are very costly irrespective of being chemically and thermally stable (Owlad et al., 2009). Aroua et al (2007) reported on polymer enhanced ultra filtration membrane for removing Cr(VI) (Chitosan,
Polyethyleneimine (PEI) and Pectin). Polymer based membrane filters generally face biofouling problem (Owlad et al., 2009). Use of liquid membranes though reported to be an effective method with high diffusion rate, they suffer by being unstable due to liquid loss and swelling of the membranes during Cr(VI) removal (Owlad et al., 2009).

The methods discussed above have several advantages. However, they remove toxic hexavalent chromium without changing the oxidation state of chromium. Unless the recovery process is efficient, remediation by these methods would not be successful.

1.8.2 CHROMIUM REDUCTION METHODS

1.8.2.1 CHEMICAL METHODS

The traditional methods use chemical agents to convert toxic Cr(VI) to non toxic Cr(III) and precipitate them as insoluble hydroxide. Reduction of Cr(VI) to Cr(III) by sulfur dioxide/sodium bisulfate followed by precipitating to Cr(III) hydroxide with the aid of sodium hydroxide/calcium hydroxide treatment generally produces high chemical sludge which is difficult for disposal (Barrera-Díaz et al., 2012). The other commonly used reducing agent includes iron(II)chloride, ferrous sulfate and sodium sulfite. Reduction rate by Iron (II) salts are reported to be high only at low pH and also produces large amounts of ferric hydroxides as sludge (Barrera-Díaz et al., 2012). When sodium sulfite is used, toxic, volatile sulfur dioxide gas is produced that cause air pollution (Barrera-Díaz et al., 2012).

1.8.2.2 ELECTROCHEMICAL METHODS

The combination of electrochemical and chemical reaction make this method to be widely used to treat solid, liquid and gas contaminated with chromium (Barrera-Díaz et al., 2012). This method is considered as adaptable and attuned method with main reagent as electron. It is generally referred as electrocoagulation and electro dissolution method. Electrocoagulation consists of two electrodes: a cathode (liberates hydrogen gas) and an anode (sacrificial electrode) that is usually aluminum or iron (Emamjomech et al., 2009). It involves two stages: [1] reduction of Cr(VI) to Cr(III); [2] precipitation. The other method generally differs with electro coagulation method
by its electro dissolution of iron (anode) under strong acidic condition followed by reduction of Cr(VI) (Lakshmipathiraj et al., 2008). Though this method is generally followed in electroplating industry, its wider application in other industrial waste water is a matter of concern as it is generally affected by change in pH and presence of other ion especially salt ions.

The different physico-chemical methods reviewed describes the available method for remediation of chromium by either removal or reduction. The methods that support reduction of hexavalent chromium have wider advantages. Moreover the available physicochemical method on reduction requires specific acidic condition for remediation. The other limitation includes the interference of other pollutants during treatment processes which actually reduce their efficiency. The generation of large chemical based sludge is the other major problem. With all this, alternate eco friendly methods have to be adopted that cause least secondary detrimental effect to the environment. The alternate biological methods that require lesser reagents other than carbon will be a viable method. Biological methods generally use microorganism like fungi, yeast and bacteria to reduce the toxic hexavalent chromium to non toxic trivalent chromium. The isolation, identification and characterization of respective species to suit local environmental or effluent condition are relatively easy and inexpensive than the other methods.