Chapter – 1

Introduction
Chapter 1

ABSTRACT

A brief review of natural, anthropogenic and industrial sources of Chromium(VI), chemistry of Chromium in soil and aquatic environment, hazardous effect of Chromium(VI), kinetics and metabolism of Chromium in human, Adsorption/ desorption of Chromium(VI) in soil and factors affecting the mobility of Chromium(VI) in soil such as clays, soil matrix and pH. Adsorption mechanism and kinetics, and some previous studies of adsorption desorption of Chromium on different adsorbent have been included in this chapter. The scope of the present work has been outlined at the end of this chapter.
One of the serious threats to our fascinating and fragile environment is the discharge of untreated effluent into the soil and water bodies. Among the various contaminants, discharge of heavy metal ions into the environment are of prime concern because of their persistent nature, toxicity, and non-biodegradability leading to ecological problems. These heavy metals which have transferred to the environment are highly toxic and can bio accumulate in the human body, aquatic life, natural water bodies and also possibly get trapped in the soil.

Soil contamination by heavy metals is extremely pernicious because these contaminants are environmentally persistent, unlike most organic contaminants, metals are generally stubborn and cannot be degraded or readily detoxified biologically. Toxic metals pose a particularly difficult long-term pollution problem [1].

The rapid development and proliferation of process industries have made wastewater treatment a major concern in industrial areas. Advances in science and technology have brought tremendous progress in many spheres of development, but in the process, also contributed to degradation of environment all over the globe due to very little attention paid to the treatment of industrial effluents. Thus the presence of metal ions in natural (mainly by volcanic activity and weathering of rocks) or industrial wastewater and their potential impact has been a subject of research in environmental science for a long time.

Chromium is one of the most commonly found metal contaminants in soil. Chromium has been extensively studied and their effects on human health are regularly reviewed by international bodies such as the WHO [2]. These Chromium compounds coming to the earth's surface not only contaminate surface water (seas, lakes, ponds and reservoirs), but can also contaminate underground water in trace amounts by leaking from the soil after rain and snow.

Elemental Chromium is a transition-group metal belonging to group VIB of the periodic table and has oxidation states ranging from –2 to +6, of which the Chromium(III) and Chromium(VI) forms are the most important. Elemental Chromium does not occur naturally in the environment. Trivalent Chromium [Cr(III)], which occurs naturally and is an essential nutrient, and hexavalent
Chromium [Cr(VI)], which, along with the less common metallic Chromium (Cr), is most commonly produced by industrial processes. Chromium(III) is essential to normal glucose, protein, and fat metabolism and is thus an essential dietary element while the Chromium(VI) is carcinogenic. Chromium(VI) compounds are strong oxidizing agents and are highly corrosive. In environment, they generally are reduced to Chromium(III) compounds. The Chromium(VI) compounds most commonly encountered in industry are potassium chromate and dichromate, chromium trioxide, sodium chromate and dichromate, calcium chromate and dichromate, lead chromate, strontium chromate, and zinc chromate [3].

Chromium is seventh most abundant elements in the earth’s crust with an average concentration of 100 mg L\(^{-1}\) [4]. Chromium has four stable isotopes with masses of 50 (natural abundance 4.35%), 52 (83.8%), 53 (9.50%) and 54 (2.37%) [5]. Chromium is the only elemental solid which shows anti ferromagnetic ordering at or below room temperature [6]. It has also high corrosion resistance and hardness. Many of its compounds are intensely colored. Because of its unique characters, Chromium was widely used in electroplating, tanning, pigments, dyes, industrial water cooling, metal finishing, magnetic tapes, paper pulp producing, photographic film, automotive parts, chemical manufacturing, wood protection, ore and petroleum refining, metallurgical and refractory producing, and other industrial activities [7-9].

1.1 Sources of Chromium(VI)

Some important sources of Chromium(VI) in Lithosphere are as given below:

1.1.1 Natural Sources

Chromium was discovered later than other metals because of its relatively low concentration in the earth’s crust-detected at approximately 100 ppm in Chromium rich rocks. Additionally, Chromium does not appear terrestrially as a native metal, but is strongly bonded to minerals in which it occurs. Naturally occurring Chromium is usually present as trivalent Chromium. Hexavalent Chromium in the environment is almost totally derived from human activities [10]. Chromium in water originates from natural sources, such as weathering of rock constituents, wet precipitation and dry fallout from the atmosphere, and run-
off from the terrestrial systems. Natural sources of Chromium accumulation in soil are due to the weathering of parent rock. 30-40% of Chromium in atmosphere is from the natural sources [11, 12]. Chromium is a naturally occurring element in rocks, animals, plants, soil, and volcanic dust and gases. In nature Chromium occurs in more than fifty different ores. The following are some important ores:

- Barbertonite: $\text{Mg}_6\text{Cr}_2(\text{CO}_3)(\text{OH})_{16}.4\text{H}_2\text{O}$
- Brezinaite: $\text{Cr}_3\text{S}_4$
- Chromite: $(\text{Mg,Fe}^{2+})(\text{Cr,Al,Fe}^{3+})_2\text{O}_4$
- Chromatite: $\text{CaCrO}_4$
- Nichromite: $(\text{Ni,CoFe}^{2+})(\text{Cr,Fe}^{3+},\text{Al})_2\text{O}_4$

Chromium minerals are generally resistant to weathering. Therefore, 75% of the annual transfer of Chromium into the environment is by mining activities [13]. Its concentrations in industrial wastewaters range from 0.5 to 270.0 mg·L$^{-1}$ [14]. The tolerance limit for Chromium(VI) for discharge into inland surface waters is 0.1 mg·L$^{-1}$ and in potable water is 0.05 mg·L$^{-1}$ [15].

In order to comply with this limit, it is essential that industries treat their effluents to reduce the Chromium(VI) to acceptable levels [16]. Central pollution control board in India has set the maximum permissible limit of chromium in waste water to be below 0.01 mg L$^{-1}$ for hexavalent Chromium and 5 mg L$^{-1}$ for the trivalent Chromium salts [17]. It is therefore important to not only recover/reuse Chromium from waste stream prior to disposal for economic reasons but also to confirm the stringent laws.

### 1.1.2 Anthropogenic Sources

Many industrial and other anthropogenic activities (e.g. disposal of products or chemicals containing Chromium, or burning of fossil fuels) are responsible for discharging huge amounts of Chromium compounds into the environment, including air, soil, and water [18].

The content of Chromium in soils is generally low. The range of mean concentrations of Chromium varies from 7 to 150 ppm and its content and
distribution in the soil mainly depends on the type of the soil’s mother rock. The presence of additional amounts of the element in the soil is caused by human activities, including emission of furnace or coke dust or combustion of fluid fuel or tannery waste water or communal solid waste. [19-21]. Chromium and its compounds are extensively used in textile, electroplating, leather tanning, metal finishing, nuclear power plant, dyeing and photography industries [22, 23]. Out of the total chrome ore production 90% is used in metallurgical industries for steel, alloy and nonferrous alloy production. Only 5% each has been used in refractory (iron & steel, cement, glass, ceramics and machinery) and chemical (leather tanning, plating, wood preservation and pigment) industries (Figure 1.1) [24].

Heavy metal release to the environment has been increasing continuously as a result of industrial activities and technological development, posing a significant threat to the environment, public and soil health [25]. Chromium is released into the environment by a large number of industries such as mining, iron sheet cleaning, chrome plating, leather tanning, wood preservation [26], electroplating, metal finishing, textile industry and nuclear power plants [27]. These industries contain Chromium(III) and Chromium(VI) at a concentration ranging from 10 to 100 mg/L [28, 29]. Long-term release of such wastewater may result in the accumulation of heavy metals in soil.

![Figure 1.1: Percentage use of Chromium in different industry.](image-url)
1.1.3 Industrial Sources

The most important industrial sources of Chromium in the atmosphere are those related to production of ferrochrome which is an alloy of Chromium and Iron containing 50% to 70% Chromium. Hexavalent Chromium is present in the effluents produced during the electroplating, leather tanning, cement, mining, dyeing and fertilizer and photography industries and causes severe environmental and public health problems [30]. The tanning process is one of the largest polluters of chromium all over the world. Most of the tanneries in India adopt the Chromium tanning process because of its processing speed, low costs, and light color of leather and greater stability of the resulting leather. In the Chromium tanning process, the leather takes up only 60–80% of applied Chromium, and the rest is usually discharged into the sewage system causing serious environmental impact. Chromium ion in liquid tanning wastes occurs mainly in trivalent form, which gets further oxidized to Chromium(VI) form, due to the presence of organic substances [31].

1.1.4 Mordant in Textile Industry

Demands of clothing and apparel increase with the improving sense of fashion and lifestyle; thus textiles are manufactured to meet the growing demand. Mordants, are substances, (such as Chromium), used to “fix” color onto the fabric. They may be are very toxic and may have a high impact on the wastewater quality. Many natural dyes (plant extracts, etc.) require a mordant and natural dyestuffs require large quantities of water for dyeing (Almost equal to or double that of the fiber’s own weight). About 80 percent of the dyestuffs stay on the fabric, while the rest go down the drain. Since Chromium is almost exclusively used as the mordant on wool, chrome dye has become essentially synonymous with mordant dye. Consequently natural dyes prepared from wild plants and lichens can have a very high impact on the environment [32].

Thousands of small-scale dyeing units, employing millions of people, generate enormous amount of polluted water. Mostly, the areas situated around industrial belts are under stress due to the continuous disposal of the untreated water. The quality of water is continuously deteriorating due to addition of toxic
dyeing effluents. Dyeing effluents from textile industries are highly toxic as they contain a large number of metal complex dyes (e.g. Chromium and cobalt complexes) [33, 34]. The high concentration of such dyes causes many water borne diseases and increases the BOD of receiving waters [35]. Hundreds of small-scale dyeing industries are facing closure since they are not treating their effluents. It is not economical for them to treat the effluent [36]. S. S. Patel et al (1999) was found that, the textile, dyeing and printing industrial effluents have an adverse effect on the soil and ground water eco systems. It is mainly due to leachates of cationic and anionic species from textiles effluents through soil strata. A comparison of collected data clearly indicates that about 3-8 folds increase in the concentration of all parameters of effluent amended soil near the industrial area [37].

Textile, dyeing and printing industrial effluent contain following metals:

Ca > Na > Mg > K > Zn > Cr > Fe > Hg > Pb > Cu > Cd > As > Ni

Ground water near industrial area

Ca > Mg > Na > K > Zn > Fe > Cr > Pb > Hg > Ni > Cu > Cd > As

Soil affected by industrial effluents

Ca > Mg > Na > K > Fe > Zn > Cr > Cu > Pb > Ni > Hg > Cd

Unless, these soils are managed properly, it may lead to severe land and ground water pollution affecting various component of the soil eco system [38].

1.2 Chemistry of Chromium in Environment

1.2.1 Chemistry of Chromium in Soil

The literature indicates that Chromium behavior in soil is complex, and depends on environment conditions such as pH, oxidation reduction potential, and ionic composition of the soil and groundwater. Very little information is available concerning the chemical form of the element in the soil, but it is generally assumed to occur as the trivalent Chromium oxide. Natural α-Al2O3 contains occasional Chromium(III) ions in place of Aluminium(III) ions. The migration of Chromium takes place only in a strongly acidic and reducing medium, where it occurs in the form of the Cr3+ cation, or a strongly basic and oxidizing medium,
where it occurs as the \( \text{CrO}_4^{2-} \) anion. Due to low solubility of its compounds and their high availability, Chromium plays an important role in the soil processes [39-41]. During weathering, Chromium oxide in rocks tends to oxidize soluble Chromium(VI) anions. Chromium(VI) is relatively stable and mobile in soils that are sandy or contain low organic matter concentration. In soils with high pH and low organic matter content, Chromium(VI) is readily mobilized by groundwater, but at lower pH and higher organic matter content Chromium(VI) may adsorb or be reduced to Chromium(III) and then adsorbed onto the soil. Chromium(VI) in soil is divided into two categories; exchangeable fraction, which is the fraction of Chromium easily removed from the soil, and non exchangeable fraction, which includes the fraction either very tightly adsorbed by the soil or precipitated on the soil [42]. Chemical and physical processes that control the rate of transport and mobility of chromium in soil include diffusion, adsorption-desorption, precipitation-dissolution, oxidation-reduction, and complexation [43].

R. J. Bartlett (1991) [44] showed that Chromium(VI) is capable of moving towards groundwater due to its extreme mobility, and it is in thermodynamic equilibrium with the atmosphere. Chromium(VI) is the product of oxidation of Chromium(III) with atmospheric oxygen and its presence is greater into the earth crust. Since the natural oxidation of Chromium(III) is extremely low, most of the Chromium(VI) found in soil and groundwater results from pollution. The Chromium(III) reactivity increase when the inert crystals and amorphous mineral are transformed into organic and hydroxide forms which are smaller and more mobile.

The equilibrium between the two Chromium forms, Chromium(VI) and Chromium(III) in soil depends upon soil physical and chemical characteristics. The oxidation process is only controlled by the reaction kinetics, due to Chromium(III) species immobility and insolubility. Chromium(III) tends to be strongly bound by soil humic acid polymers, and this affinity restricts the availability of Chromium(III) to be oxidized and reduce the organic matter decomposition [45, 46]. The presence of manganese oxide in soil favors trivalent Chromium oxidation, thus increasing the hazards connected to hexavalent Chromium contamination of groundwater.
Some previous studies found that the stable Chromium(III) form in soil is oxidized to Chromium(VI) by manganese dioxide, which serves as the electron acceptor in Equation 1.1. The rate of Chromium(III) oxidation by β-MnO$_2$ was found to increase with decreasing pH [47, 48]. Chromium(III) concentration, pH, and the amount of initial available β-MnO$_2$ surface are the parameters controlling the degree of oxidation [49]. The amount of Chromium(III) oxidized to Chromium(VI) was proportional to the manganese reduced. The following oxidation equation was proposed:

$$\text{CrOH}_2^+ + 1.5 \text{MnO}_2(s) = \text{HCrO}_4^- + 1.5 \text{Mn}^{2+}$$

Both oxidation of Chromium(III) and reduction of Chromium(VI) can be thermodynamically favorable in soil. The transformation of Chromium(VI) to Chromium(III) within soils is likely to occur in the presence of electron donors such as Fe (II) [50]. The rate and amount of reduction of Chromium(VI) in soil is difficult to predict. Reduction of Chromium(VI) with organic compounds to insoluble Chromium(III) forms has been studied by several workers. Organic matter present in clays provides a sufficient source of electrons for reduction of Chromium(VI) to Chromium(III). Another source of Chromium(VI) reduction to Chromium(III) is from Fe(II) in hematite and biotite. Past studies with pure mineral phases have shown that even the small amounts of Fe (II) contained in hematite and biotite can reduce aqueous Chromium(VI) species to Chromium(III), resulting in the precipitation of (Fe,Cr)(OH)$_3$ [48]. Reduction of chromate by the ferrous ions produced by dissolution of the ferrous iron components of hematite and biotite in acidic media is described by the following reaction:

$$3[\text{FeO}]_{\text{biotite}} + 9\text{H}^+ + \text{HCrO}_4^- = \text{CrOH}_2^{2+} + 3\text{FeOH}^{2+} + 3\text{H}_2\text{O}$$

1.2.2 Chemistry of Chromium in Aquatic Environment

Oxidation reduction processes play a major role in the mobility, transport, and fate of inorganic and organic chemical constituents in natural waters. Of the possible oxidation states of Chromium, only hexavalent and trivalent Chromium are of interest in environmental systems. Chromium speciation in groundwater is affected by pE and pH conditions (Figure 1.2) [51]. Chromium in natural waters exists in two oxidation states: +3, Chromium(III) or
trivalent form; and +6, Chromium(VI) or hexavalent form. Chromium (VI) species are anionic (i.e., HCrO$_4^-$ and CrO$_4^{2-}$) and are generally mobile in most neutral to alkaline systems. The proportion of each ion in solution depends on pH and total chromium concentration. The following are the important equilibrium reactions for different Chromium(VI) species in aquatic environment [52]:

$$H_2CrO_4 = H^+ + HCrO_4^- \quad \text{log} \, K \,(25 \, ^\circ C) \quad -0.8 \quad (1.3)$$

$$HCrO_4^- = H^+ + CrO_4^{2-} \quad \text{log} \, K \,(25 \, ^\circ C) \quad -6.5 \quad (1.4)$$

$$2HCrO_4^- = Cr_2O_7^{2-} + H_2O \quad \text{log} \, K \,(25 \, ^\circ C) \quad 1.52 \quad (1.5)$$

$$HCr_2O_7^- = H^+ + Cr_2O_7^{2-} \quad \text{log} \, K \,(25 \, ^\circ C) \quad 0.07 \quad (1.6)$$

Equations 1.3, 1.4, and 1.6 shows that the predominant species present, as a function of the pH, are $H_2CrO_4$ at pH less than 0.8, $HCrO_4^-$ at pH between 0.8 to 6.5, and $CrO_4^{2-}$ at pH above 6.5. Equation 1.5 does not contain any $H^+$ terms, and therefore, in a certain pH range (2-5) this reaction is nearly independent of pH and depends only on total Chromium(VI) concentration. When the concentration of chromium exceed 10 mM and under acidic conditions bichromate ($HCrO_4^-$) polymerizes to form dichromate ($Cr_2O_7^{2-}$). Chromium(VI) species are strong oxidants that are reduced to the trivalent state by aqueous Fe(II) and organic compounds [52-54]. As the pH becomes lower, Chromium(VI) species are removed from solution by adsorption onto positively charged sorption sites [55]. The dominant Chromium(III) species occurring in groundwater also depend on pH. Apparent stability constants (298 K, K=0.75) calculated for pertinent reactions, relevant for Chromium(III) speciation are [56]:

$$Cr^{3+} + H_2O = CrOH^{2+} + H^+ \quad \text{log} \, K \,(25 \, ^\circ C) \quad -4.4 \quad (1.7)$$

$$Cr^{3+} + 2 H_2O = Cr(OH)_2^{2+} + 2 H^+ \quad \text{log} \, K \,(25 \, ^\circ C) \quad 10.6 \quad (1.8)$$

$$Cr^{3+} + 3 H_2O = Cr(OH)_3^{3+} + 3 H^+ \quad \text{log} \, K \,(25 \, ^\circ C) \quad -19.2 \quad (1.9)$$

$$Cr^{3+} + 4 H_2O = Cr(OH)_4^{4-} + 4 H^+ \quad \text{log} \, K \,(25 \, ^\circ C) \quad -28.2 \quad (1.10)$$

$Cr(OH)_2^{2+}$ is the dominant species in natural ground waters with a pH between 6-8, $CrOH^{2+}$ and $Cr^{3+}$ predominate in more acidic environment. $Cr(OH)_3^{3+}$ and $Cr(OH)_4^{4-}$ predominate in more alkaline environment (Figure 1.2). Chromium
(III) solubility is limited due to the formation of hydrous oxides, Cr(OH)$_3$(s) and chromite (Fe,Cr)(OH)$_3$(s), and the strong tendency to adsorb onto clays and other solid phases. Chromium(III) can also form soluble organic complexes, particularly under acidic conditions. However, Chromium(III) could be converted to the more soluble Chromium(VI) if the redox state changes from reducing to highly oxidizing [47, 57].

![Figure 1.2: A simplified Pourbaix diagram for chromium species at 150°C and [Cr(aq)]$_\text{tot}$ = 10$^{-8}$ [58, 59].](image)

### 1.3 Hazardous Effects of Chromium(VI)

In the array of heavy metal ions, chromium is of special interest because it is an essential nutrient as well as a carcinogen [60]. Dietary deficiency of Chromium(III) has found to cause faulty sugar metabolism [61], although in combination with insulin, it removes glucose from the blood and also plays a key role in fat metabolism [62]. On the other hand, Chromium(VI) is lethal to human system because of its mutagenic and carcinogenic properties [63, 64]. Trivalent
Chromium is an essential micronutrient whereas Chromium(VI) is listed as a Group 1 human carcinogen by the International Agency for Research on Cancer [65].

1.3.1 Acute (Short Term) Health Effects

Short-term effects of Chromium(VI) exposure (for example, from chromic acid droplets or chromate dust) include eye irritation and respiratory irritation, sneezing, or sensitization; acute exposure to high levels of Chromium(VI) can produce nervous system damage and liver disorder [66]. In high concentrations, acute inhalation can cause ulcers in the nasal septum. In sensitive individuals, inhalation of Chromium(VI) can cause an asthma attack. If very small quantities are ingested, the body converts it to the trivalent form in the stomach. In larger quantities or concentrations, however, ingestion of hexavalent Chromium compounds can result in acute gastroenteritis, vertigo, gastrointestinal hemorrhage, convulsions, ulcers, kidney damage or failure, and liver damage or failure; approximately 1 g of potassium chromate is considered a lethal dose. Significant acute exposure of the skin to Chromium(VI) can cause burns, liver damage or failure, kidney damage or failure, and anemia [67].

1.3.2 Chronic (Long Term) Health Effects

Hexavalent Chromium compounds are highly toxic when ingested or inhaled. Carcinogenesis caused by Chromium(VI) may result from the formation of mutagenic oxidative DNA lesions following intracellular reduction to the trivalent form [68]. Excessive exposure to toxic Chromium(VI) results in various health problems such as chronic ulcers, dermatitis, hemorrhage, and pulmonary cancer [67]. Chromium(VI), generally occurs in the form of chromate \((\text{CrO}_4^{2-})\) and dichromate \((\text{Cr}_2\text{O}_7^{2-})\), has the ability to diffuse through cell [69] and modifies DNA transcription process which can lead to digestive tract and lung cancer [70]. If inhaled through the mouth, it can cause periodontitis and gingivitis. Impacts of chronic skin exposure include dermatitis, hypersensitivity reactions, eczema, and kidney or liver damage. The characteristic lesions resulting from Chromium(VI) exposure are referred to as "chrome holes" or "chrome ulcers." Chronic eye exposure can result in conjunctivitis [71].
1.3.3 Exposure Routes

Ingestion of Chromium(VI) in drinking contaminated groundwater or surface water. This is still being debated within the scientific community. Dermal contact through bathing or washing in Chromium(VI) contaminated water is another exposure pathway. Chromates can enter the bloodstream through breaks in the skin. \(\text{CrO}_4^{2-}\) blood poisoning occurs when \(\text{CrO}_4^{2-}\) destroys red corpuscles. Inhalation is also an important human exposure pathway; however, it is less likely to be associated with exposure to Chromium(VI) contaminated soil and groundwater and more likely associated with industrial processes such as welding, cutting, heating of Chromium alloys, and work related practices. With low pH rain or fruit juice (orange juice and lemon juice), the Chromium can be leached off the wood surface [72].

1.3.4 Worker Health

Workers, rather than consumers, have the highest risk of adverse health effects from Chromium(VI) exposure. The industries with the greatest risk of occupational exposure to Chromium(VI) are chrome electroplating, stainless steel welding, metal coating and painting, printing, textiles, leather tanning, wood preservation, and cement or masonry work. Inhalation risk may be from fumes (welding), mists or droplets (electroplating, spray painting.) Dermal exposure can result from contact with fluids, such as those used in electroplating, or materials containing Chromium(VI), such as wet cement; smoking can increase the risks from Chromium(VI) exposure [73].

1.3.5 Public Health

Chromium may enter in human body through food, water, air, or adsorption through the skin when they come in contact with humans in, industrial, or residential settings. Industrial exposure accounts for a common route of exposure for adults [74]. Chromium is found naturally in the soil in trace amounts, which pose few problems. Exposure may occur from natural or industrial sources of Chromium. The average daily intake from air, water, and food is estimated to be less than 0.2 to 0.4 \(\mu\)g, 2.0 \(\mu\)g, and 60 \(\mu\)g, respectively [75].
1.3.6 Environmental Hazards

There are both naturally occurring and anthropogenic sources of Chromium compounds in the air, soil, and water. Natural sources include volcanic activity and the weathering of Chromium-containing rock. The dumping of industrial waste materials significantly increases Chromium concentration in soil and is usually accompanied by groundwater contamination [76]. Chromium in the air is in the form of particles or droplets, which may be transported by wind and deposited onto soil or water. The behavior of Chromium compounds in soil and water is complex. Chromium (VI) can leach out of soil into groundwater and migrate over time [73, 77]. Factors that determine whether the Chromium is in trivalent or hexavalent form in different environmental media (air, soil, surface water, ground water) include pH, oxygen levels, temperature and the presence of other chemicals and organic matter [78].

1.4 Kinetics and Metabolism of Chromium in Human

In mammals, Chromium(III) is an essential trace element involved in lipid and glucose metabolism. It is usually considered that almost all the Chromium in food is present as Chromium(III) [79]. About 0.5-1% of Chromium(III) present in the normal diet is absorbed [80]. Adsorption of ingested Chromium(VI) compounds is greater than for Chromium(III) compounds, ranging from approximately 2-8%, although most of ingested Chromium(VI) is considered to be reduced to Chromium(III) in the stomach prior to absorption [79, 81]. The behavior and toxicity of Chromium is strongly dependent on the valency, physical-chemical properties of the substance, the particle characteristics and the route of exposure/administration.

Chromium(VI) chromate ions are transported into cells, whereas Chromium(III) compounds enter into cells by passive diffusion and phagocytosis. Furthermore, water soluble Chromium(III) aerosols of respirable size are more efficiently absorbed from the respiratory system than from the gastrointestinal tract, with approximately 5% being absorbed within hours of exposure, followed by further slow systemic absorption over weeks or months. Uptake of deposited and retained insoluble Chromium(III) oxide particles is a very slow process and
particles containing Chromium may be retained in the lung for years following occupational exposure. In contrast, once deposited in the lungs, Chromium(VI) compounds are generally transferred to the systemic circulation more readily than Chromium(III) compounds [79-82].

Chromium(VI) is more efficiently adsorbed through the skin than Chromium(III) compounds. Chromium compounds are widely distributed in the body, with a greater distribution reported following exposure to Chromium(VI) compounds compared to Chromium(III), reflecting the greater tendency of Chromium(VI) to cross plasma membranes. Chromium(VI) is unstable in the body and is reduced to Chromium(V), Chromium(IV), and ultimately to Chromium(III) by endogenous substances such as ascorbate and glutathione and it is believed that the toxicity of Chromium may result from damage to cellular components during this process (e.g. through the generation of free radicals) [12].

1.5 Adsorption Desorption of Chromium(VI) in Soil

Various methods of Chromium removal include filtration, chemical precipitation, adsorption, electrodeposition and membrane systems or even ion exchange process. Among these methods, adsorption is one of the most economically favorable and a technically easy method [82]. In most soil environment adsorption is the dominating speciation process and thus the largest fraction of heavy metal in a soil is associated with the solid phase of that soil. Pollution problem arise when heavy metals are mobilized into the soil solution and taken up by plants or transported to the surface/ground water. The properties of the soil are thus very important in the attenuation of heavy metals in the environment. The solubility of heavy metals in soil is controlled by reactions with solid phases [38]. Once introduced into the soil, the heavy metal species undergo several possible fates including adsorption/desorption reactions, precipitation/dissolution reaction, plant uptake and mobility through soil profile.

Adsorption is a major process responsible for accumulation of heavy metals. Therefore the study of adsorption processes is of most importance for the understanding of how heavy metals are transferred from a liquid mobile phase to the surface of a solid phase [83]. There are two general surface complexes
formations are described by the configuration geometry of the heavy metal at soil surface. These include inner- and outer-sphere surface complexes and are defined by the presence, or absence, of the hydration sphere of the adsorbate molecule upon interaction. When at least one water molecule of the hydration sphere is retained upon sorption, the surface complex is referred to as outer-sphere. When the ion is bound directly to the adsorbent without the presence of the hydration sphere, an inner-sphere complex is formed [84-87].

Chemicals like heavy metals once introduced to the environment by one particular method may spread to various environmental components. Heavy metals may chemically or physically interact with the natural compounds, which change their forms of existence in the environment. In general they may react with particular species, change oxidation states and precipitate [88]. Heavy metals may be bound by particular natural substances, which may increase or decrease mobility. Studying the dissipation of heavy metals is called speciation [89, 90].

The most important interfaces involved in heavy metal adsorption in soil are predominantly inorganic colloids such as clays [91], metal oxides and hydroxides [8], metal carbonates and phosphates. Also organic colloidal matter of detrital origin and living organisms such as algae and bacteria provide interfaces for heavy metal adsorption [92-95]. Adsorption of heavy metals onto these surfaces regulates their solution concentration, which is also influenced by inorganic and organic ligands. Those ligands can be of biological origin such as humic and fulvic acids [96, 97] and of anthropogenic origin such as NTA, EDTA, polyphosphates, and others [98-101], which can be found frequently in contaminated soils and wastewater.

The most important parameters controlling heavy metal adsorption and their distribution between soil and water are soil type, metal speciation, metal concentration, soil pH, solid: solution mass ratio, and contact time [102-105]. In general, greater metal retention and lower solubility occurs at high soil pH [106]. To predict fate and transport of heavy metals in soils both conceptual and quantitative model approaches have been developed. These models include the determination of the nature of the binding forces, the description of the chemical
and physical mechanisms involved in heavy metal–surface reactions and the study of the influence on variations of parameters such as pH, Eh, ionic strength and others on adsorption [83].

Some important factors influencing chromium mobility in soil are discussed here:

1.5.1 Clays

Several low cost adsorbents such as agricultural/industrial wastes and natural/synthetic clay minerals have been used as effective adsorbents for removal of heavy metals, organics and radionuclides [107, 108]. Hence, in the past decades, clay minerals have been used as effective adsorbents for heavy metal removal in water treatment because of their strong ion-exchange and complex formation abilities with the heavy metals [109, 110]. Knowing the sorption and desorption characteristics of the heavy metals on the clay mineral, will in no small measure, aid in modeling the behavior of the soil when contaminated by these heavy metals. It will also be achieved through studying adsorption and desorption behavior of clay minerals [108].

The clay buffer capacity and the initial pH play an importance role in the mobility of the heavy metals in the clay. Alkaline pH condition enhances the precipitation of the heavy metals, thereby reducing their mobility [111]. Clay minerals exhibit a strong affinity for heavy metals. They possess a wide pore size distribution, ranging from micro (< 20Å) to mesopores (20-500 Å). The ionic charges on the clay surface can also increase the adsorption capacity by attracting oppositely charged polluting substances and convert them into harmless or easily removed forms. A number of clay minerals have been investigated for water and waste water treatment, including sepiolite [112], kaolinite [113], montmorillonite [114], smectite [115] and bentonite [116].

1.5.2 Soil Matrix

Soil is a very complex heterogeneous medium, which consists of solid phases (the soil matrix) containing minerals and organic matter and fluid phases (the soil water and the soil air), which interact with each other and ions entering
the soil system [117]. The ability of soil to adsorb metal ions from aqueous solutions has consequences for both agricultural issues such as soil fertility and environmental questions such as remediation of polluted soil and waste deposition. The solid state of soil composes an average of 45% of soil bulk. It consists of mineral particles, organic matter and organic-mineral particles. They all play a very important role in giving the soil the ability to adsorb, exchange, oxidise, reduce, catalyze and precipitate chemicals and metal ions [90].

Heavy metals added to soil will normally be retained at the soil surface. Movements of metals into other environmental compartments, i.e., ground water, surface water, or the atmosphere, should be minimal as long as the retention capacity of the soil is not exceeded. The extent of movement of a metal in the soil system is intimately related to the solution and surface chemistry of the soil and to the specific properties of the metal and associated waste matrix. The retention mechanisms for metals added to soil include adsorption of the metal by the soil solid surfaces and precipitation. The retention of cationic metals by soil has been correlated with soil properties such as pH, redox potential, surface area, cation exchange capacity, organic matter content, clay content, iron and manganese oxide content, and carbonate content. Anion retention has been correlated with pH, iron and manganese oxide content, and redox potential.

Changes in the soil environment over time, such as the degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes also may enhance metal mobility. The extent of vertical contamination is intimately related to the soil solution and surface chemistry of soil matrix with reference to the metal and waste matrix. It has been found that the relative mobility of nine metals through Montmorillonite and Kaolinite to be \( \text{Cr(VI)} > \text{Se} > \text{As(III)} > \text{As(V)} > \text{Cd} > \text{Zn} > \text{Pb} > \text{Cu} > \text{Cr(III)} \) [118, 119].

1.5.3 Soil pH

Soil pH appeared to be greatest determination of Chromium solubility and mobility in a light textured sandy soil [120]. The mobility and bioavailability of heavy metals increases with decreased soil pH [121-123], thus enhancing the
uptake of heavy metals by plants and thereby posing a threat to human health [124, 125]. Thus the soil pH was found to play the most important role in determining metal speciation, solubility from mineral surfaces, movement, and eventual bioavailability of metals, due to its strong effects on solubility and speciation of metals both in the soil as a whole and particularly in the soil solution [126, 127].

The soil components responsible for element adsorption include, soil humic substances, phyllosilicates, carbonates and variable charge minerals (constituents such as Fe, Al, Mn and Ti oxides, short-range ordered aluminosilicates as well as phyllosilicates coated by OH-Al or OH-Fe species whose charge varies with the pH of the soil solution). Unlike phyllosilicates, the variable charge minerals (crystalline and short range ordered Fe, Al, Mn-oxides, allophanes, imogolite) strongly retain heavy metals for their dependency on pH. On these materials a hydroxylated or hydrated surface, positive or negative charge is developed by adsorption or desorption of H⁺ or OH⁻ ions [87].

The pH at which the net variable charge on the surfaces of these components is zero is called the point of zero charge (PZC). The reported PZC of Fe-oxides, range from pH 7.0 to 9.5, whereas that of Al-oxides ranges from pH 8.0 to 9.2 [128-130]. Variable charge minerals selectively adsorb polyvalent cations, even when their surfaces are positively charged (solution pH values lower than the point of zero charge [PZC] of the adsorbent). Some previous studies suggested that chromate forms an outer-sphere complex on the surfaces of Fe and Al oxides. However, spectroscopic studies have shown that chromate forms inner-sphere complexes on goethite [131, 132]. The pH value of the investigated soil is naturally alkaline (8.2) which promotes heavy metals precipitation and adsorption onto the clay surface. Soil organic matter plays an important role in the adsorption of heavy metal ions even in soils where its value is very low [85].

1.6 Adsorption Mechanism and Kineticts

The adsorption efficiency is often described by means of adsorption equilibrium isotherms and kinetic studies. Chemical kinetics can be defined for the soil chemical interaction as the study of the rate of chemical reaction and of molecular process by which the reaction occurs where transport is not limiting
The application of kinetic theories to heterogeneous soil constituents is one of the most important and challenging areas to be investigated. Chemical reactions in soils are generally heterogeneous, soil liquid reactions involve a solid component of the soil and the soil solutions. In the agriculture fields, interaction of soils with fertilizers ions, pesticides, insecticides, chemicals in irrigation water etc lead to several ion-exchange, adsorption, desorption and transport processes accompanied by displacement of solutes and adsorbates in a liquid phase, solid-phase and at the interface. The processes of ion-exchange, simultaneous adsorption and desorption of species bonded to charged surface of soil by electrostatic forces. Some methods commonly adopted to study kinetics of soil chemical interactions resulting in adsorption-desorption are as follow:

### 1.6.1 Kinetic Methodologies

Kinetics deals with description of time dependent processes which are path dependent. Methods helpful in obtaining kinetic data for studying various types of reaction in soil are mainly the following:

(i) Relaxation methods

(ii) Batch methods

(iii) Flow methods

Relaxation and batch methods are most suitable for adsorption studies only, while flow methods are widely applied for desorption and leaching studies. A good review on these methods is by D. L. Sparks (1989) [134]. R. A. Ogwada et al (1986) [135] have investigated the effect of kinetic methodologies and degree of agitation on rate parameters using five different methods. In the static technique, there was no mixing, in continuous flow and batch method agitation was done. The stirred method was based on stirring of the mixture. In a vortex batch technique, the mixture was rapidly mixed on a vortex mixer. Results showed that significant diffusion exist in the static and miscible displacement methods because of limited mixing.

Flow methods have been used in a number of kinetics studies on soil and soil constituents [136]. Flow methods have also been used on soil reactions by D. L. Sparks et al (1981), [137] and S. C. Hodge et al (1987) [138] for solute transport in soils.
1.6.2 Adsorption Equilibrium Study

Adsorption is usually described through an isotherm. The adsorption isotherm indicates how the adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [139]. The adsorption isotherm is useful for representing the capacity of an adsorption catalyst for providing description of the functional dependence of capacity on the concentration of pollutant. The steeper the isotherm, the more effective is adsorption that is, the sharper the rise of the isotherm to a given ultimate capacity as concentration increases, the higher will be the effective capacity at the concentration level desired for the treated water.

Experimental determination of the isotherm is a routine practice in evaluating the feasibility of adsorption process. The adsorption isotherm relates to an equilibrium condition, however any practical detention time used in most treatment applications do not provide sufficient time for true equilibrium to obtain. Rates of adsorption are thus significant, as more rapid the approach to equilibrium, the greater is the fraction of equilibrium capacity utilized in a given contact time.

Equilibrium adsorption isotherm is of important in designing the adsorption system. Several isotherm equations are available and three important isotherms i.e. Langmuir, Freundlich and Temkin isotherms have been used extensively by early researchers in this field [140].

Some of the studies conducted on adsorption-desorption of Chromium (VI) on different adsorbents have been summarized in Table 1.1.
### Table 1.1: Some Previous Studies on Adsorption – desorption of Chromium (VI)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Adsorbent</th>
<th>Experimental method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Cellulose –clay composite biosorbent</td>
<td>Batch method</td>
<td>[141]</td>
</tr>
<tr>
<td>2.</td>
<td>EDTA modified cross linked chitosan resin</td>
<td>Batch method</td>
<td>[142]</td>
</tr>
<tr>
<td>3.</td>
<td>Eucalyptus bark</td>
<td>Batch method</td>
<td>[31]</td>
</tr>
<tr>
<td>4.</td>
<td>Activated carbon developed from Tamarind wood activated with Zinc Chloride</td>
<td>Batch method</td>
<td>[143]</td>
</tr>
<tr>
<td>5.</td>
<td>Tamarindus indica seeds</td>
<td>Batch method</td>
<td>[144]</td>
</tr>
<tr>
<td>6.</td>
<td>Polypyrrole magnetic nanocomposite</td>
<td>Batch method</td>
<td>[145]</td>
</tr>
<tr>
<td>7.</td>
<td>Waste Marigold Flowers</td>
<td>Batch method</td>
<td>[146]</td>
</tr>
<tr>
<td>8.</td>
<td>Flyash</td>
<td>Batch method</td>
<td>[36]</td>
</tr>
<tr>
<td>9.</td>
<td>Seeds of Artimisia absinthium</td>
<td>Batch method</td>
<td>[147]</td>
</tr>
<tr>
<td>10.</td>
<td>Modified and unmodified bentonite clay</td>
<td>Batch method</td>
<td>[148]</td>
</tr>
<tr>
<td>11.</td>
<td>Divinylbenzene copolymer resin</td>
<td>Batch method</td>
<td>[149]</td>
</tr>
<tr>
<td>No.</td>
<td>Material Description</td>
<td>Method</td>
<td>Reference</td>
</tr>
<tr>
<td>-----</td>
<td>--------------------------------------------------------------------------------------</td>
<td>------------</td>
<td>-----------</td>
</tr>
<tr>
<td>12.</td>
<td>Mangrove leaf powder</td>
<td>Batch method</td>
<td>[150]</td>
</tr>
<tr>
<td>13.</td>
<td>Sulfuric acid - modified Avocado seed</td>
<td>Batch method</td>
<td>[67]</td>
</tr>
<tr>
<td>14.</td>
<td>Activated Carbon derived from Water Hyacinth</td>
<td>Batch method</td>
<td>[151]</td>
</tr>
<tr>
<td>15.</td>
<td>Activated Carbon primed from sugarcane bagasse</td>
<td>Batch method</td>
<td>[152]</td>
</tr>
<tr>
<td>16.</td>
<td>Chitosan powder</td>
<td>Batch method</td>
<td>[76]</td>
</tr>
<tr>
<td>17.</td>
<td>Organobentonite</td>
<td>Batch method</td>
<td>[153]</td>
</tr>
<tr>
<td>18.</td>
<td>Admixtures of rice husk, shredded tyre and fly ash</td>
<td>Batch method</td>
<td>[154]</td>
</tr>
<tr>
<td>19.</td>
<td>Natural clay used as Landfill liner</td>
<td>Batch method</td>
<td>[155]</td>
</tr>
<tr>
<td>20.</td>
<td>Chemically modified Okra Powder</td>
<td>Batch method</td>
<td>[156]</td>
</tr>
<tr>
<td>21.</td>
<td>One step steam pyrolysis corn cobs activated carbon</td>
<td>Batch method</td>
<td>[157]</td>
</tr>
<tr>
<td>23.</td>
<td>Soil Colloids</td>
<td>Batch method</td>
<td>[158]</td>
</tr>
<tr>
<td>24.</td>
<td>Palm tree branches</td>
<td>Batch method</td>
<td>[66]</td>
</tr>
</tbody>
</table>
1.7 Scope of the Work

The main objective of the present study was to understand the process of the adsorption desorption of the Chromium(VI) onto the soil. The study aimed to investigate natural processes involved in adsorption of Chromium(VI) through physical and chemical processes. The effect of variation of different parameters on migration and adsorption of Chromium(VI) on soil has also been included. The studied parameters mainly consist of initial Chromium(VI) concentration, contact time, particle size of soil, amount of soil, pH of solution, and temperature. The experiments were conducted and the best fitted kinetic model and adsorption isotherm for the adsorption of Chromium(VI) onto the soil evaluated. The parameters which influence mobility of Chromium(VI) in the subsurface soil and groundwater have been studied to predict further contamination trends under various soil conditions. Thermodynamic parameters, for instance enthalpy, Gibbs free energy and entropy were evaluated to predict feasibility of adsorption processes.

Remediation of the Chromium(VI) contaminated sites is often a costly and time consuming process. Understanding of the physico-chemical processes which affect adsorption and chemical state of Chromium(VI) is required to work out any preventive/remedial strategy for remediation of Chromium contaminated soil.

This study emphasizes to determine remediation of already contaminated sites and to work out possible preventive measure to protect soil and water resources from getting contamination. Results may also provide guidance for selection of appropriate and cost-effective remediation methods for contaminated sites, and the study will help in designing the remedial/precautionary measure to check the environmental pollution through soil and ground water. The study may also be helpful for Pollution Control Board in framing guide line for disposal of chemical waste from industries.
1.8 References


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Chapter 1


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